

Historic, Archive Document

Do not assume content reflects current scientific knowledge, policies, or practices.

Reserve
aTP676
.M32

A SURVEY ON RESEARCH POSSIBILITIES
FOR ANIMAL FATS
TO
U. S. DEP'T. OF AGRICULTURE

JOHN W. McCUTCHEON
CONSULTING CHEMIST
475 FIFTH AVENUE
New York, N. Y.

Project No. 86
Contract No. A-1s-32689
SEPTEMBER 1951

AD-33 Bookplate
(1-43)

NATIONAL

**A
G
R
I
C
U
L
T
U
R
A
L**



LIBRARY

TABLE OF CONTENTS

	Page
INTRODUCTION	1
SECTION 1	3
Fats; purification, separation & chemical modification- Statistics on Tallow and Grease	
Research on Fats	17
Rendering	17
Processing methods to purify fats	18
(a) Bleaching	18
(b) Alkali refining	19
(c) Deodorizing	19
Processing methods to separate the glycerides --	19
(a) Solvent extraction-Solexol Process	19
(b) Solvent crystallization	20
(c) Pressing	21
Processing methods to chemically modify a fat --	21
(a) Interesterification	21
(b) Double bond modification	21
(c) Double bond addition	22
SECTION 2	23
Fatty acids and derivatives	23
Processing methods to obtain fatty acids	23
Processing methods to chemically modify fatty acids	26
A-Carboxyl Modification	26
(1) Esters	26
(2) Salts; - Inorganic, Soluble	26
" " Metallic	35
Organic	39

U.S. DEPT. OF AGRICULTURE
NATIONAL AGRICULTURAL LIBRARY

JAN 10 1992

CATALOGING PREP.

FOR ADMINISTRATIVE USE ONLY
NOT FOR PUBLICATION
OR DISTRIBUTION

TABLE OF CONTENTS CONT'D.

(3) Amides	42
Preparation of	42
Reactions of	43
Uses of	43
(4) Nitriles	51
Reactions of	52
(5) Amines	60
Reactions of	64
Uses of	66
(6) Alcohols	72
Production of	72
Uses of	74
(7) Miscellaneous Carboxyl Modified Derivatives	76
B-Internal Chain Modification	76
(1) Elaidinization	76
(2) Addition Reactions	77
(3) Fission of "A" Unsaturated Acids "Oleic" "B" Saturated Acids Stearic, Palmitic	77 78
(4) Substitution Products	80
Halogenation	80
SECTION 3	86
Edible Animal Fat Products	86
Lard as a Shortening and Margarine Material	94
SUMMARY	97

INTRODUCTION

In conformity with the above numbered contract a list of approximately 163 companies and individuals was selected for interview. These were taken from a category of producers of fatty acids and derivatives, producers of fats, users of fats and derivatives, producers of the active ingredients of synthetic detergent research institutes and associations connected with fats and oils and individuals who by their published papers and otherwise have shown interest in this subject. As the work progressed certain new companies and individuals were added to this list and certain individuals and companies already listed were not available through one reason or another.

In preparation for the interviews a four-page questionnaire was drawn up although at the time this was done it was not anticipated that the type of questioning would lend itself too readily to this method of approach. A copy of the questionnaire is enclosed in the Appendix. The outline questionnaire was taken on each interview, and used as a guide to the questions. However, the nature of the individual business and the degree of willingness to discuss research determines to a large degree, the selection of the questions asked. In most cases the desired information was developed in such a way that it was best noted on the reverse side of the questionnaire. This is understandable and was anticipated. Almost all interviews have been handled by the undersigned personally and in such a way that no feeling of antagonism was engendered. Since it was not possible to force answers and since the very nature of the inquiry was highly confidential, it was considered important to develop a friendly spirit and to leave the way open for further discussion either by personal contact or by correspondence.

The general reception at all companies was good. The information obtained was in general sketchy. The large companies were very reluctant to discuss what they were doing unless it had already been released for publication. Smaller companies with less to lose perhaps because they have done less, are more prone to discuss what they have in mind for research and what they would desire. The response depends considerably on the temperament of the person interviewed. In each case the person interviewed was determined by the president or head of the Company to whom the original inquiry was addressed, and consisted, in the majority of

cases, of the Heads of the Research Departments. Private organizations, institutes and universities were most cooperative and willing to discuss their work. Unfortunately, their research was usually directed along lines not specific to this undertaking.

Since the companies research interests are very much tied up in their patent work it was considered desirable to study the list of companies originally selected and to examine their patent structure. This was done for the period 1930 to 1950 inclusive and approximately 3000 patents were noted in the process, although only a fraction of these had any true value as far as this report is concerned.

The investigation has shown that there is no unified research program on tallow or its derivatives except that being done by the large packers. In some cases even their interest is divided. For example, Armour and Company is not only interested in the expanded uses for tallow but is also actively engaged in the processing of Tall Oil, particularly as a raw material for the production of non-ionic synthetic detergents. Two such type products are Triumph and Giant.

Swift and Company have not been very active in the field of tallow fatty acid derivatives but they expect to become more interested shortly. Wilson and Company make derivatives of tallow fatty acids in a small way at their Philadelphia factory. The renderers as a group are not doing any research on tallows or greases although a program has been started by the American Meat Institute on proteins. Individually the renderers are small without research facilities. Only a few companies are large enough to do research and most of the work which is being done in such places is directed to the processing of tallow and grease and has little direction towards expanding its uses.

The report is divided roughly into three sections.

- Section (1) deals with fats, methods of obtaining, purification, separation and chemical modification.
- Section (2) deals with fatty acids and derivatives; methods of manufacture, purification, separation and chemical modification.
- Section (3) deals with edible tallow and lard.

SECTION 1

FATS; PRODUCTION, PURIFICATION, SEPARATION
AND CHEMICAL MODIFICATION

To obtain a proper balance as to the opportunities for expansion in the inedible animal fat and fatty acid field, it is necessary to have some understanding of the present statistics of the industry. Factory consumption of tallow and grease in soap for the period 1936 - 1949 is given below.

TABLE 1

CONSUMPTION OF INEDIBLE TALLOW & GREASE IN SOAPS

1936 - 1949 (Thousands of lbs.)

A. INEDIBLE TALLOW(1)

Year	Total Consumpt.	Consumpt. in Soap	% of Total going to soap	Ave.(2) Price
1936	725,974	660,020	91.0	6.6
1937	675,918	613,509	90.8	8.3
1938	764,041	702,267	92.0	5.6
1939	874,099	785,041	89.9	5.5
1940	884,685	786,456	89.0	4.5
1941	1,190,542	1,057,303	88.8	7.6
1942	1,342,396	1,188,923	88.5	9.2
1943	1,081,744	896,286	82.8	8.6
1944	1,210,625	1,005,777	83.1	8.6
1945	1,210,834	952,334	78.5	8.6
1946	1,165,218	871,968	74.8	11.2
1947	1,344,636	1,108,909	82.4	19.2
1948	1,211,995	980,670	80.8	16.0
1949	1,141,420	961,505	84.3	6.3

(1)

B. GREASE

Year	Total Consumpt.	Consumpt. in Soap	% of total going to soap	(3) Price Ratio	
				Ave. Price	Grease Tallow/(2)&(3)
1936	204,532	98,714	48.3	5.7	1.16
1937	215,651	94,247	43.8	7.3	1.14
1938	182,767	96,356	52.7	4.8	1.17
1939	210,911	120,856	57.0	4.8	1.14
1940	356,513	256,886	72.1	4.0	1.13
1941	470,214	310,487	66.0	7.0	1.08
1942	517,369	338,974	65.5	8.8	1.04
1943	677,504	463,811	68.4	8.4	1.02
1944	712,039	523,972	73.5	8.4	1.02
1945	627,937	411,600	65.5	8.4	1.02
1946	511,389	337,871	66.0	10.9	1.03
1947	536,962	416,838	77.6	18.0	1.07
1948	569,947	470,784	82.6	13.6	1.18
1949	522,268	384,092	73.6	5.3	1.19

(1)

C. INEDIBLE TALLOW & GREASE

Year	Total Consumpt.	Consumpt. in Soap	% of Total Going to Soap
1936	930,506	758,734	81.5
1937	891,569	707,756	79.4
1938	946,808	798,623	84.4
1939	1,085,010	905,897	83.5
1940	1,241,198	1,043,342	83.8
1941	1,660,756	1,367,790	82.2
1942	1,859,765	1,527,897	82.1
1943	1,759,248	1,360,097	77.5
1944	1,922,714	1,529,749	79.6
1945	1,838,771	1,363,934	74.3
1946	1,676,607	1,209,839	72.0
1947	1,881,598	1,525,747	81.0
1948	1,781,942	1,451,454	81.4
1949	1,663,688	1,345,597	80.9

- (1) Bureau of the Census Animal & Vegetable Fats & Oils 1936-40, 1940-44, 1942-46 and 1945-49.
 (2) Prime tallow in carlots Chicago, from Fats & Oils Situation #147, Feb. - March 1951, P 21.
 (3) Yellow grease, loose, Chicago. From FOS 147-P 21.

The data of this table reveals the importance of soap as a market outlet for both grease and inedible tallow. In 1946 for example when only 950 million lbs. of inedible tallow and grease was factory consumed by industry, soap consumption accounted for over 758 million pounds, or 81.5% of the total. In 1949 when consumption of these two materials had increased to over 1663 million lbs., soap consumption still kept pace with a usage of over 1345 million lbs. or 80.9% of the total. This high diversion of inedible tallow and grease to soap use has remained fairly constant over the years with the exception of the war and immediate post war years as the tabulation under C of Table 1 indicates.

Inedible tallow has been displaced to a small extent by grease as a soap making fat, the usage having declined from approximately 90% to 80% while that of grease has risen from about 50 to 70%. The principle rise in grease usage took place during the war years when tallows were in short supply, and in the face of an adverse price structure, column 6, Table 1 B., which at that time was fixed. The continued use of grease in high percentage in the post war years may be attributed to better processing, better methods of handling and to a more favorable price relationship to inedible tallow, exceeding even the pre-war ratio.

At the present moment however, the relation of inedible tallow and grease to one another, is less important than their combined usage in soap, which in 1949 was 80.9% of their total consumption. Of the total consumption of inedible tallow and grease 169,378,000 lbs. or 10.1% was converted to fatty acids, leaving 148,713,000 lbs. or 8.9% for use in sulfonated oils, greases, textile cutting oils, etc. The greatest concern therefore is for the use of tallow in soap and the diversion of its uses from this product because of synthetic detergents. Tariff reports show that total production (100% active basis) of surface active agents including an almost constant 40 million lbs. of sulfonated oils has more than tripled in the last six years.

1945	-	184,442,000 lbs.
1946	-	242,174,000 lbs.
1947	-	291,161,000 lbs.
1948	-	374,715,000 lbs.
1949	-	429,890,000 lbs.
1950	-	676,346,200 lbs.

The estimate of bulk detergents for 1949 is placed at 1.2 billion lbs. of which 900 million are retail products almost exclusively within the class of granulated detergents. The Census

475 FIFTH AVENUE NEW YORK 17, N. Y.

of Manufacturers report for 1947 with added fat content (estimated by the writer) is as follows.

TABLE 2

(In Millions of lbs., - 1947)

	<u>Type of Product</u>	<u>Amount</u>	<u>Fat Content</u>
1	Toilet Soap	555	500
2	Granulated Soap	1522	1000
3	Laundry Bar Soap	791	382
4	Soap Chips	427	350
			2232
5	Washing Pdr. Abrasive Cleaners Liquids & Paste Mechanics & Medicated	795	121
			2353

which indicates that very probably 2.4 billion (1.5 from Table 2, #2 / 0.9 from Est. 1947 bulk prod.) pounds of powdered detergents were sold of which 0.9 billion or 37% was synthetic. The estimated retail and industrial split of bulk synthetic detergents calculated on a 35% active basis is as follows:

TABLE 3*

Bulk Synthetic Detergent Production in Millions of Pounds

	1939	'40	'41	'42	'43	'44	'45	'46	'47	'48	'49	1950
Retail	100	100	100	100	100	100	150	300	525	775	825	900
Industrial	70	80	80	80	100	140	150	150	175	200	250	300
Total -	170	180	180	180	200	240	300	450	700	975	1075	1200

This agrees with the American Soap Association reports fairly well, when it is considered that in 1948 only 17 companies were reporting production and in 1950 % active in retail synthetics
*Data obtained from trade estimates.

has fallen to about 22% due to the great climb of heavy duty products such as TIDE, FAB AND SURF, etc.

TABLE 4*

(Net weight basis as sold in 1000's of lbs.)

	<u>1948</u>	<u>1949</u>	<u>1950</u>	<u>1st Half</u> <u>1951</u>
Hard Soap Production	2,491,380 (60)	2,440,024 (92)	2,439,259 (85)	1,104,625 (85)
Synthetic Detergent Production	401,685 (17)	702,136 (37)	1,070,688 (34)	611,528 (37)

* Data from reports of Association of Am. Soap & Glyc. Prod. Inc.
Bracketted numbers refers to companies reporting.

There is no indication that synthetics have reached a saturation point. Summarized data covering 9 widely separated cities (Omaha, St. Paul, Indianapolis, Milwaukee, Columbus, Sacramento, Fresno, Modesto and Rockford) and the questioning of 862,000 families gives weighted average figures as follows:

TABLE 5

	<u>1947</u>	<u>1948</u>	<u>1949</u>	<u>1950</u>
Soaps for fine fabrics				
Synthetic Detergents used % of total	28.6	31.2	34.5	37.3
Soaps for dishes				
Synthetic detergents used as a % of total	36.4	44.2	54.0	56.8

The steady climb in these two important categories of use is taken to indicate an average increase of about 4% in retail products equivalent to 50,000,000 lbs. (since we can consider most of the increase due to retail sales.) This represents an equivalent soap powder displacement, which on a 60% fat basis represents

30 million lbs. of soap fat displaced per year. It is estimated that on a gross retail production of 900 million lbs. 540 million lbs. of fats would be displaced representing at best 350 million lbs. of tallow and grease (since such products will run about 65% tallow and grease and the balance foots and vegetable oils.) Although the total fats and oils going to synthetics in 1950 was placed at 65 million lbs. (Fats & Oils Situation October, 1950) it is estimated that not more than 10 million would be used in retail detergents so that fat diverted to this use is negligible. A fallacy of thought is that this loss of tallow and grease business could be regained by causing synthetics to be fat based. Taking the alkyl sulfate as a base example, the tallow derivative contains 79% fat, and a lauryl sodium sulfate 74% fat. A 22% active detergent would therefore contain approximately 17% fat so that 900 million lbs. of such detergent could be made from 153 million lbs. of fat, and the majority of this would have to remain coconut oil on present processes. However, such a gain is not to be ignored and data following under Soaps & Halogenated Substitution Products has something to say along this line. Actually, fat has not made much headway into retail detergents. Only one product appears on the present market - TIDE. Its estimated fat usage per year has been placed at 60 million representing a production of about 350 million lbs. or about 13 million cases. (This information was not received direct.) Up to 50% tallow or grease can be substituted for coconut oil in this formula and there is good reason to believe this is being done at the present time. This would mean an additional use for tallow or grease up to about 25 - 30 million lbs.

The above discussion is designed to lay the ground work for an approach to profitable lines of research. It shows that the use of tallow per se, is still very important, that detergents have made the situation alarming and that a solution to the problem is not going to be found by converting such products to a fat base. The use of fat has been so well established that only major chemical modifications or diversions of other oils to new fields will be of interest. Such processes will be examined, particularly in reference to soap uses itself. In respect to the 10.1% (of total tallow and grease) diverted to fatty acids, the multiplicity of uses possible is most interesting and considerable space is given to their discussion. In 1949 394,826,000 lbs. of fatty acids were produced from vegetable animal and fish oil sources plus an estimated 200,000,000 lbs. of fatty acid in continuous soap processes which do not enter census figures. This is a healthy 600 million lbs. It is believed that the established use of soap is such that the diversion of 300-400 million lbs. of tallow to new uses would very greatly stabilize the market. Doubling or tripling fatty acid production would be such a move. This is by no means beyond reason.

Present continuous fat splitting capacity is estimated from data gathered in this survey, at 400 million lbs; Twitchell fat splitting capacity is estimated at 300 million, for a total of 700 million lbs. This would be a minimum figure since soap plant capacity was not available and was therefore conservatively estimated at 200 million lbs.

To provide a background of data for proper evaluation of fatty acids and derivatives the following is presented.

TABLE 6

Production of Fatty Acids 1949. Census Data.

1. Coconut fatty acids from coconut oil - - - - 37,642,000 lbs.
2. Vegetable oil fatty acids from miscellaneous oils such as linseed, castor, cottonseed, soyabean refined coconut oil, etc. - - - - 17,174,000 lbs.
3. Vegetable oils fatty acids from foots principally cottonseed foots & soyabean foots - 134,561,000 lbs.
4. Fatty acids from tallow - - - - - 119,015,000 lbs.
5. Fatty acids from grease - - - - - 50,363,000 lbs.
6. Fatty acids from hydrogenated animal fats - 20,138,000 lbs.
7. Fatty acids from misc. primary fat sources excluding vegetable but including marine oils 4,583,000 lbs.
8. Fatty acids from refuse fats chiefly recovered palm oil from the tin plate industry - $\frac{1}{2}$ - - 11,350,000 lbs.

Sub Total - - - 394,826,000 lbs.

To this must be added fatty acids split by continuous processes and converted directly to soap and reported as consumed in soap 200,000,000 lbs.

Grand Total approximately - - - 600,000,000 lbs.

Vegetable oil foots are used largely as a source of fatty acids. The 134,561,000 lbs. in the table could be about doubled if necessary since about 50% goes to the soap kettle in some form or another. On the other hand, coconut, tallow and grease fatty acids are not derived to any great extent from the foots but are largely derived from the fats themselves. The foots

are consumed in soap, with small exception. Tall oil is being used to the full extent of its production which amounted to 250 million lbs. in 1949, 310 million in 1950 and probably 330 million lbs. in 1951. Its recovery is fairly well established at the present time and although there is a steady growth noted over the three years given, it is felt that present production is approaching a peak limit. In the first place, it is a secondary product dependent on the production of pulp from the southern pine. This yields about 60 lbs. of tall oil per ton of pulpwood processed. Not all producers are recovering their tall oil, but at the present rate of pulpwood production, which averages 550,000 tons per month, the total tall oil available would be not over 400 million lbs. per year. Present recovery is therefore over 80% of the available supply. Secondly, there is some possibility of southern hardwoods being used to replace the pine. Development along these lines will reduce tall oil production since such woods have no recoverable rosin and fatty acids. Thirdly, the extension of tall oil recovery to pulping operations on northern pines has not to date been very promising due to the low fat content of these woods. A few mills in certain sections are finding recovery profitable, but it appears very doubtful if this will develop into any large scale source of supply.

With these factors in mind, it is doubtful that tall oil production will increase by more than 25% over its present rate of production during the next ten years.

Considering therefore both vegetable oil foots and tall oil as additional sources of fatty acids it must be concluded that any large increase in fatty acid production over present rates in excess of about 200 million lbs. would have to come from tallow. The basic acids with which we are directly concerned therefore are stearic, palmitic and oleic. To these must also be added the derived acids from the fission of oleic acid, namely polargonic and azelaic.

As a further help in discerning productive research, the following uses of animal fatty acids are given, based on the Census data, as modified by the interviews.

TABLE 7

Uses of Animal Fatty Acids

(A) STEARIC (49,363,000 lbs. 1949)

1. Rubber, chiefly synthetic. (Single pressed)	25.9%
2. Chemicals, including edible emulsifiers & ester plasticizers, etc.	13.3%
3. Cosmetics, shaving soaps (Triple pressed)	11.8%
creams, etc. " "	8.4%
4. Lubricating greases, etc.	6.4%
5. Polishes, floor waxes,	6.4%
6. Candles	4.8%
7. Mould release powder with plastics, rubber, etc.	3.6%
8. Metal working. Buffing, compounds (single pressed)	2.1%
9. Water proofing, cement. Metal salts.	1.9%
10. Ceramics	1.9%
11. Resins, as plasticizers & as chemical ingredient	1.8%
12. Textiles, in cationic softeners, waterproofing etc.	1.6%
13. Pharmaceutical	1.6%
14. Protective coatings, rubber, cloth, etc.	1.7%
15. Paint and varnish, as flatting agent, etc.	1.0%
16. Wire drawing	1.0%
17. Crayons & chalk, phonograph records, as binder etc.	.9%
18. Matches, putty, etc.	.8%
19. Sulfonated acid, as emulsifier	.2%
20. Paper sizing	.2%
21. Insulation linoleum, leather, etc.	.3%
22. Glue and adhesives	.1%
23. Chlorinated products as plasticizers	.1%
24. Printing inks	.1%
25. Misc. uses unaccounted.	2.4%
	<hr/>
	100.0%

(B) OLEIC (46,168,000 lbs. 1949)

1. Soap. Liquid soaps. This material is at present meeting stiff competition from tall oil, synthetic detergents & other vegetable oil fatty acids in this field which last outsell oleic 3/2	28.0%
2. Chemicals including ore flotation derivatives, synthetic detergents and other surface active agents	28.0%
3. Textiles including 2.1% of total as sulfonated product, balance as softeners	9.6%
4. Cutting oils, metal treating, etc.	8.6%
5. Lubricants and greases	3.9%
6. Polishes, shoe, furniture etc.	3.8%
7. Asphalt	3.0%
8. Protective coatings	3.0%
9. Rubber as part of the formula	2.5%
10. Putty, caulking compounds	2.9%
11. Petroleum de-emulsifiers	1.7%
12. Leather processing	2.6%
13. Cosmetics and pharmaceuticals	.4%
14. Printing inks	.3%
15. Hydraulic brake fluids, etc.	.2%
16. Insulation	.1%
17. Core oils	.1%
18. Alkyd resins	.2%
19. Miscellaneous	1.1%
	<hr/> 100.0%

(C) MIXED (22,030,000 lbs. 1949)

1. Lubricants and grease	34.8%
2. Soap - used by small manufacturer to avoid equip.	21.7%
3. Rubber	20.2%
4. Chemicals (emulsifiers, etc.)	12.1%
5. Paint and varnishes	4.2%
6. Protective coatings	1.5%
7. Plastics as part of formula	1.5%
8. Leather	1.4%
9. Metal work, mold lubricants, etc.	1.4%
10. Textile, fiber softening, etc.	.8%
11. Miscellaneous	.4%
	<hr/> 100.0%

D. Hydrogenated. (20,138,000 lbs.)

These are manufactured to substitute for the higher priced stearic where the higher content of true stearic acid is unimportant or is to be preferred. Such substitutions occur chiefly to replace stearic acid in rubber and in chemical derivatives.

1. Chemicals	67.2%
2. Paint and Varnish	8.8%
3. Lubricants and grease	7.7%
4. Rubber	5.7%
5. Soap	4.7%
6. Textile (Sulfonated products)	2.9%
7. Linoleum and oil cloth	.7%
8. Metal processing, mold, wire drawing, etc.	.6%
9. Pharmaceuticals	.2%
10. Glues	.2%
11. Protective coatings, paper, plastics	.2%
12. Miscellaneous	1.1%
	<hr/>
	100.0%

The limited time available for this report, made it imperative to screen out research which had little or no bearing on the increased tonnage use of tallow. For this reason, a whole class of derivatives may be omitted from this report as for example such biologically interesting compounds as the sterols. This does not mean however that the research on these products was not examined. In addition, products or classes of products which had only a present minor use and which did not appear promising, were dealt with briefly so that the resultant report would emphasize the positive rather than the negative avenues of development. Two major conclusions from the interviews were:

- (1) The ill effect instability of tallow price has on research and
- (2) The lack of a coordinated group of persons to direct research on tallow, grease and lard.

Companies who deal exclusively with fats are not aware of the significance of this fluctuation as a drawback to the use of their products. Such companies would be the renderers such as Darling & Co. and the fatty acid producers, such as Gross and Company. The companies having products which are both fat and

petroleum derived are sensitive to such fluctuation in price. For example scapers who are now making non-fat synthetics are very pleased with the price structure of their new raw materials as compared with fats. It is quite possible that this may actually influence their research and production. As an example, the Alrose Chemical Company started business about 1945 heavily interested in fat-based emulsifiers for the cosmetic trade. Usage for these products has expanded to such an extent that sales to the cosmetic industry is but a small fraction of total output. In spite of this success however, with such type products, the company has entered into a new field of activity, namely the manufacture of benzene derivatives whose purpose and use is entirely unrelated to the surface active field. Questioned on this point they frankly admitted that price instability of fats had a lot to do with this change of products. This example is typical of many companies visited, although probably not so openly admitted.

Companies that deal primarily in petroleum or coal tar derivatives look upon fat research with great reluctance. A process that looks good today will be shelved tomorrow, and vice versa. As soon as money is invested in a plant the company stands to lose terrifically with a slight change in price. The furfural process of Pittsburgh Plate Glass Co. is a prime example. A plant designed for up-grading of soybean oil glycerides and dependent on a 3-4¢ margin between soybean oil and linseed oil, was forced to shut down when the margin became 2¢, as in February, and 2-3/4¢, as of July 13, 1951.

No better example of price fluctuation in the fat field is available than that noted during the course of this contract. In February of 1950 the price for No. 1 tallow was around 12¢. Then for about 4 months it was at an unprecedented low of about 5¢. In the fall it rose until those interviewed wanted to know why there was any need for a program on tallow as it was in short supply at 15¢ or so. It finally rose to 19¢, a ceiling was put on it at 15¢ and now after 18 months it is back to 8¢.

The problem of tallow and grease price fluctuation is very complex and stems partly from its tie in with oils and fats in general, and also to the fact that the market is dependent for pricing on the flow of only a small portion across its threshold. There is considerable material sold on contract (probably the majority) based on the market price as of day of delivery, or any other suitably designated day. This situation is extremely bad for any intensive research problem. No evidence was noted however of any attempt on the part of large users to make purchases other than in an orderly way to meet their week to week requirements.

We now come to the second major conclusion from the

475 FIFTH AVENUE NEW YORK 17, N. Y.

interviews, namely the lack of a coordinated research program. This is essential to any program. The diverse interests must pass through a common melting pot and be balanced so that so much work is done on oleic and so much on stearic so that one does not make oleic one year and give away the stearic and the next year make stearic and give away the oleic. To expect others to do this research and give it away is beyond reason. In the first place, any company doing research is doing it for its own interests. If it is studying oleic for example, it is not concerned whether it obtains it from tallow, vegetable oils or tall oil. Work that is done is fenced in with patents. The respect for private property is excellent, but imagine a community built with no plan where everyone staked a claim and built his house where he pleased. Not even a street or a road could be set up. As long as tallow had a steady and expanding market in soap and related products, there was little apparent need for research. This situation is no longer tenable.

The framework for organized research exists in the various renderers associations and in particular in the National Renderers Association. For various reasons, mainly financial, little work to date has been carried out on fats. One program started under the direction of the American Meat Institute, deals with the protein content of scrap. The renderers themselves, being small in general, have little facility for doing research and in this respect differ very much from the producers of other domestic oils such as cottonseed, linseed, soybean, etc. In the latter case the American Oil Chemists' Society acts as a clearing house for independently developed research. There is nothing in this latter organization which could absorb the type of research program envisioned here. The Fatty Acid Producers group within the American Soap & Glycerine Producers Association, is too recently organized for an appraisal of its value to such a program.

The following suggestions represent a brief synopsis of opinions expressed during the interview by a wide range of interests.

(1) Direction of the research might conceivably be done by a committee selected from industry. The research proper could be handled in the laboratories of the producing and consuming companies or research institutes, and published through normal channels.

(2) The industry should establish a secretary and full time director to contact industry and act as nerve center for all activity. The operation of the Tall Oil Association is an interesting type of such organization.

(3) The group should be industry wide and should embrace producer and consumer as well.

(4) It should avoid patents on work done or should keep such arrangements to a minimum.

(5) It should correlate and suggest the direction of work only.

(6) It should reduce duplication of work by making known periodically, work being done under its direction or suggestion and by having new work checked and published by a few companies.

A study of existing groups and their method of working would be beneficial. Suggested organizations include the ASTM Committee 12 on methods of analysis, the Tall Oil Association, The American Soap & Glycerine Producers Association, The Tin Committee at the Battelle Memorial Institute, the A.P.I. committee on petroleum hydrocarbons and the American Meat Institute at Chicago.

The ASTM Committee 12 might indicate by way of example how a phase of work, such as on detergents, supplements the work of the Am. Oil Chem. Soc. without duplication; the Tall Oil Assoc. might suggest how the office of a research director for an organization is developed; the Am. Soap & Glycerine Producers Association could point out one method of raising funds without publicizing the strength of individual members, the Tin Committee would undoubtedly have some very useful information regarding the handling of patents developed by cooperative research; the A.P.I. committee could show how both industry and university may be harmonized together on a single project; and lastly the American Meat Inst. may point out the method of organizing a research group to act for one or more sections of industry while maintaining its corporate structure within the confines of a university.

The feelings of the industry on this subject were briefly as follows:

LARGE FAT and FATTY ACID PRODUCERS - We feel money spent in our own laboratories pays greater dividends than money spent outside. In general they are not interested.

THE RENDERER - Not equipped generally for research. Their chief difficulty is fees. No one wants his neighbor to know how much business he is doing. This can be avoided by having an independent accounting firm examine the books of each company and assess a fee proportionate to its financial status,

475 FIFTH AVENUE NEW YORK 17, N. Y.

to meet the required budget. The amount so specified may be kept confidential between the accounting firm and the individual company.

THE INSTITUTES - Ready at any time for a research fellowship. This is merely a business proposition to them.

THE UNIVERSITIES - Ready to carry on any research problem within their scope of interest. Usually this scope is limited to fundamental research.

LARGE USERS OF FATS - Like the packer, the general attitude is that their own research organization is sufficient.

The obstacles for positive action are considerable and a protracted period of 5% tallow would probably be required as a goad to constructive thinking on this subject.

RESEARCH ON FATS

1. RENDERING

The methods of rendering have been well standardized. The quality of the product of dry rendering practiced by the renderers in general, is subject to abuse by the operators through faulty control. This is not something new of course. Procter & Gamble have endeavored to maintain good relationships with these renderers and have a team of four or five men who do nothing but visit and instruct them in the better methods of operation. Procter and Gamble have issued a small booklet on the subject called "Better Rendering" designed as a text for this operation. Lever Bros. (U.S. 2,455,374) mention hydrated silica in 0.1 - 5% as an aid to improving the color of the rendered product. As Lever Bros. are not renderers, it appears possible that this patent is designed as a friendly gesture toward the renderer. Solvent rendering is being used extensively in the mid west and to some small extent in the east (Rubin, New York city) to reduce the fat in cracklings from 7% to about 3%.

2. PROCESSING METHODS TO PURIFY FATS

(a) Bleaching.

Bleaching processes are generally adsorption ones using activated clays. No startling development has been noted but Mr. Blair of Procter & Gamble pointed out that over the years the quality of bleaching clays has steadily improved. The decolorization of tallow by the Solexol system (U.S. Pat. 2,454,638 and 2,467,906) is quite satisfactory, but in order to make it commercially useful there should be a spread of 2¢ per lb. between Fancy and #1 grade. This allows about 1½¢ per lb. operating and overhead costs plus about ½¢ allowance for a small foots loss. On a 5¢ tallow this foots loss would shrink considerably so that the operating margin between Fancy and #1 grade tallow on such basis would approach 1½¢. Unfortunately the margin between grades shrinks with low prices, so that the Solexol process offers the least help to the renderer at a time when he most requires it. Lever Bros. at Baltimore had the first commercial installation but have been using it intermittently. Three plants for tallow decolorizing, have been built.

Swift and Co.,	Chicago	100 tons per day
Lever Bros.	Baltimore	125 " " "
Refining Inc.	Cincinnati	60 " " "

Total --- 285 tons " "

The Furfural Process (Pittsburgh Plate Glass)
(U.S. Patents 2,200,390-1, 2,278,309, 2,291,461, 2,313,636, 2,316,512, 2,390,528 and 2,423,232) modified to include naphthol, is claimed useful as an oil decolorizer. It has not been used on tallow as far as the writer is aware and there is nothing to recommend it over the M. W. Kellogg Solexol Process with its more simple, one solvent process.

In regard to chemical bleaching - this is done in a small way. The sodium chlorite and chlorine dioxide method of the Mathieson Chemical Co. (Stossel, U.S. Pat. 2,431,842 and Hempel, U.S. Pat. 2,430,675) has caused quite a stir in the commercial field through its use by renderers. Procter & Gamble claim that soap made by such bleached fats revert and that the practice is unethical, since their contract with suppliers covers only unprocessed material. Levers and Colgate make no special

objection. The Mathieson Company claim successful use of the process in renderers plants over a number of years. They claim it is adaptable to pipe line bleaching by a continuous method and that soap does not revert unless the tallow is over bleached, so that chlorosubstitution products are formed by the prolonged contact between fat and chlorine. Under such circumstances there is good reason to believe that reversion can occur, although insufficient work has been done to put the point beyond dispute. This process as a method for tallow and tallow fatty acids should be investigated more fully. The Mathieson Company have not done a complete research job on this method by any means.

H₂O₂ as a bleach on acids has been admitted by Becco Company but they did not know how it was used. Possibly they refer to Lever Brothers who have Brit. Pats. 577,879-80. The claim is made that the soap stock does not revert.

Chemical bleaching, except on specialty compounds is not favored by the soap industry.

(b) Alkali Refining.

This is relatively unimportant to tallow and grease. Losses are low since well rendered tallow contains little mucilage matter. Since the foots are used as low grade soap stock there is small incentive to keep losses down by such methods as centrifuging, etc.

(c) Deodorizing.

This steam distillation method has been greatly improved in the past 20 years by use of tighter equipment, higher vacuums, deaerated and superheated water, and drop tanks for cooling before filtering. The most recent device is the semi continuous plant of Girdler and described in their bulletins. The application of deodorization to lard is easy and as satisfactory as with any other fat.

3. PROCESSING METHODS TO SEPARATE THE GLYCERIDES

(a) Solvent Extraction - Solexol Process.

This process is the same as that mentioned above under decolorization. The fat and propane are passed countercurrent to one another through a large diameter column at a definite temperature, pressure and ratio of solvent to fat. The coloring matter, saturated glycerides, unsaturated

Glycerides are classified all have different chemical properties so that a variety of products may be obtained simply by changing the conditions of temperature, pressure, and the thoroughness of the column. It is possible for example to separate tallow into a bleached fraction and a color body fraction. This is the procedure when the Solexol process is used for decolorizing tallow. The color bodies are removed as a bottom fraction from the column. Under other conditions of operation it is possible to include in the bottom fraction color bodies plus highly unsaturated. The top fraction may be made to contain the more saturated glycerides and the vitamins. By using several columns it is possible to separate all four fractions. During a visit to the J. Howard Smith plant at Keansburg, New Jersey, the plant was operating to separate Menhaden oil of iodine value 180, into fractions of iodine value 155 and 205 with one pass. This 70-ton per day plant cost \$1,500,000 and operated as a glyceride fractionator at 15 to 18 per cent including royalty charges. No color bodies were removed, hence no bleaching loss was present as in the case of decolorizing tallow, to which the next figure.

The process has little to recommend the use for tallow processing for two reasons. First, the separation of the individual glycerides is not as clear cut as that obtained on the fatty acids, and secondly, a modified propane crystallization process, about to be described, can accomplish the same separation at a lower cost.

(b) Solvent Crystallization.

This process, developed by H. W. Kellogg, is known as the Destearinizing Process. The solvent propane is used, as in the Solexol process, but the resemblance of the two processes end there. In the Crystallizing or Destearinizing process the oil-propane mixture is batch chilled to -25°C or lower, held at that temperature for a finite period to promote crystal formation and then vacuum filtered as through an Oliver filter press at a continued low temperature. The J. Howard Smith plant at Keansburg, N. J. had such a unit operating on fish oils to separate 180 iodine valued glycerides into two fractions having iodine values of 155 and 205 respectively. It is thus seen that the Solexol and Destearinization process was used to accomplish the same work on Menhaden oil, although the Solexol process, by its ability to decolorize and remove vitamins is more versatile. The plant cost of the Destearinizing unit was \$600,000 for a 50-ton per day plant. Total operating cost was placed at 0.50¢ per lb. which is considerably less than for the Solexol plant. In respect to tallow, grease and lard, this

type plant has a large potential use as a means of preparing lard oil and oleo stearin. At the present time, a pilot scale plant of this type is in use at Swift & Co., Chicago. It is believed to be in successful operation. The process has much to recommend it from a cost point of view.

(c) Pressing

Used on lard for the manufacture of lard oil, also stearin etc. The method is standard but is probably obsolete now, in view of Swift's experience.

B. PROCESSING METHODS TO CHEMICALLY MODIFY LARD

(a) Interesterification.

This process is relatively unimportant as far as tallow, grease and lard is concerned. It is doubtful if the improvement for example in a lard would warrant the expense of the operation. Procter and Gamble are very active, patent wise, in this field.

(b) Double Bond Modification.

This is relatively unimportant to this project. Oleic acid can be converted to palmitic acid easily, and at one time such a process was in operation commercially in France. During the course of this investigation one of those interviewed, mentioned a patent he had on this process for tall oil as if the idea was new. Elaidinization is unsatisfactory as it is not a complete reaction, stopping at the 2/3rd. mark. The best catalyst, selenium, is also poisonous although Dutch patents appear from time to time. Dutch patent 51,865 (1942) suggests 0.01 to 0.05% selenium. A Lever Bros. patent (Zeils, U.S. Pat. 2,468,799) mentions the use of sulphur in the hydrogenation catalyst to increase the yield of iso acids during hardening of a shortening. This is a novel idea and is worthy of some study but would not be applicable to a lard based shortening due to the low I.V. of the starting base. Conjugation and polymerization is not a part of tallow or grease chemistry, but such processes have been used to eliminate the polyunsaturates from a tallow in order to increase the purity of the derived red oil. Goebels (Emery Industry, J. Am. Oil Chem. Soc. 24 65-8 (1947)

suggests polymerization with 1-5% water, below decarboxylation temperatures and at high pressures in the presence of hydrogenation catalysts.

(c) Double Bond Additions.

Hydrogenation is the most important and is well known. (1) Its use on tallow as a means of preparing pure oleic is useful but difficult to carry out economically in present batch equipment. (2) Lard has a variable unsaturation which requires just a touch of hydrogen to bring it to a uniform product. Although Dr. Kraybill of the American Meat Institute insists that the presence of some linoleic in the finished product is of great benefit from a nutrition point of view, I am of the opinion that this is fortuitous to the present method of making a lard compound, that is, by mixing fully hydrogenated lard with unhydrogenated material as was done in the early days of shortening manufacture. If a method were available to uniformly hydrogenate lard at small expense, to an iodine value just low enough to insure the absence of linoleic acid, then I feel sure, the arguments is favor of leaving such highly unsaturates in the lard would be weak compared to the advantages to be gained in stability, by taking them out.

There is a need under both 1 and 2 above for a continuous process of hydrogenation, using a fixed catalyst and controlled by automatic means. A new source of hydrogen is available to fat processors - from thermal decomposition of NH_3 . This is being widely used by Armour, Procter & Gamble and others where the volume of gas required would not warrant a full scale propane plant, with its accompanying large capital outlay. Of course, hydrogen from such a decomposition is only economical where the usage is low, since the production of one volume of nitrogen for every three volumes of hydrogen, necessitates a periodic purge of gas, with accompanying loss of hydrogen as well. The utilization of such mixed gases with intermittent purging still remains obscure and indefinite.

Lever Bros. (Brit. 578,102 and U.S. Pat. 2,437,705-6) continue to accomplish several steps such as elaidinization and decolorization during hydrogenation. I believe this is a backward step in processing technique, since it adds more complications to an already complicated process and reduces its chances of being put on a continuous basis. Step by step continuous processes are generally preferred.

SECTION 2

1. PROCESSING METHODS TO OBTAIN FATTY ACIDS

The Twitchell process for fat splitting is now obsolete. Present fatty acid production is split approximately 400 million lbs. per year obtained by continuous splitting of fats and 200 million by Twitchell splitting. The patents for continuous hydrolysis are numerous and are held by Colgate, Procter & Gamble and Emery with cross licensing. Procter & Gamble heat their tower externally, Colgate and Emery heat internally. A lone patent by Swift is interesting just because it stands alone (U. S. Pat. 2,489,713.) The Bradshaw (Du Pont) patent (U.S. Pat. 2,271,619) for alcoholysis of glycerides to simple esters is worthy of study in view of the possibilities of making the process continuous. Colgate show their interest by a large number of U.S. Patents 2,383,601-2, 2,383,579, 2,383,632-3, 2,383,580-1, 2,383,614, 2,383,596 and 2,383,599.

A recent patent for splitting tallow is by Gunther, (to Industrial Patents Corp. U.S. Pat. 2,401,756) using Skellysolve K and concentrated NaOH at 400° F. for 7 min. at 100 psi. This patent is very similar to Kokatnur U.S. Pat. 1,813,454 which was never successfully applied on a commercial scale.

Distillation, either continuous or batch is the most common way of purifying fatty acids. There is probably no other piece of equipment in a fatty acid plant which is so affected by methods of operation and by the design of the plant itself. All modern plants of any sized production are generally continuous. Where separation of fatty acids is desired, the still is equipped with a fractionation column also, generally of about 30 theoretical plates, and capable of separating oleic and stearic from palmitic to the extent of 90% or better. No development in fat chemistry has progressed further in the past 20 years than this phase of processing. The most modern still uses very little steam to assist volatilization of the acids but an extremely high vacuum. One of the better types of stills (Potts et al, Armour & Company U. S. Pat. 2,224,925, 2,224,984, 2,224,986, 2,322,056 and 2,450,611-2) employs a separate stripping tower using steam plus a fractionation column where the vacuum is as low as 2 mm. or less and no steam is used. Procter & Gamble, in their non fractionating continuous flash-film still, designed for their continuous soap making operation, employ pressures as low as 0.2 - 0.3 mm. and no steam.

The cost of distillation is quite low as far as plant operation is concerned. For example continuous distillation of tallow fatty acids are estimated on a $2\frac{1}{2}$ ton per hour plant as follows:

Cost in \$ per 1000 lbs.

Labor	0.40
Services, steam power, water, etc.	0.13
Overhead	0.40
Repair and Maintenance	0.10
Amortization of plant over 10 yr.	0.50

\$1.53 (0.15¢ per lb.)

To this must be added the loss due to polymerization, oil residues etc. It is in this type of loss where a still will make or lose money for its operator and where the degree of fat splitting is significant.

Still design will continue to improve and become more uniform. Probably the next step in fatty acid separation will come through the increased use of distilling the esters when it becomes more feasible to produce them through alcoholysis etc. Only one firm is doing such to date - the Eldorado Oil Company in San Francisco. The advantages of such procedure over straight fatty acid distillation are, greater stability of product during intermediate stages of manufacture, and lower capital cost of equipment through the use of less expensive acid resisting alloys.

Separation of the fatty acids by pressing is now obsolete. The method is being rapidly replaced as equipment wears out. Solvent crystallization methods developed through petroleum de-waxing techniques, are fast becoming important. There are two chief methods which differ only in the solvent used - the Emery Process - using aqueous alcohol (U.S. Pats. 2,293,676, 2,298,501 and 2,352,160.) The alcohol-fatty acid mix is chilled in indirectly cooled mechanical heat exchangers of special design. The secret of good crystal formation is to have the acids present in reasonable agreement to their natural eutectic and to have a slight amount of neutral fat present, 0.2 - $3\frac{1}{2}\%$ (Emery U.S. Pat. 2,421,157.) The Texas process, (Gee, Texaco Development Co. U.S. Pat. 2,450,235) uses acetone and is the process presently employed by Armour & Company. They claim (Armour U.S. Pat. 2,443,184) that removal of the short chain acids improves crystallization. Their cooling is similar to Emery's except that the refrigerant passes directly around the jacket of the mechanical heat exchanger. Wilson and Company (Spannuth, U.S. Pat. 2,505,012)

have a solvent process also, and have been experimenting on the use of the Girdler Votator as a mechanical heat exchanger. As of the date of the interview, Wilson did not have a plant in operation on a crystallizing process. The crystals in both the Emery and Texaco methods are filtered through a continuous Oliver type press and are washed on the press screen with fresh solvent. The Texaco process can use low temperatures (-40°) to separate oleic from linoleic (Towne-Texas Co. 2,459,054) although Armour has not done this so far. For this reason, many (including Swift) consider the acetone method as more versatile and useful, than the alcohol process.

The destearinizing plant of the M. W. Kellogg Co. using propane, has been mentioned as a possible one for use on fatty acid separation. Considerable research data has been accumulated on this from laboratory experiments and the method has been used by Swift and Co. on an experimental basis. Liquid extraction processes such as the Furfural Process and Soloxol Process have not to date been used for this purpose although the Furfural Process of Pittsburgh Plate Glass has been mentioned (Gloyer Ind. & Eng. Chem. Feb. (1948) as a method for separating fatty acids. The process in such a case must contain naphthol. A study of the data would make it unattractive as designed at present.

A new method of separation not applied as yet commercially, is chromatographic separation. This process has long proven very useful as a laboratory tool. It may be applicable industrially with proper automatic control. Sun Oil Company has recently put the first plant of this kind into operation in Pennsylvania, for the removal of benzene from petroleum oils. See also Tous et al, *Anales fis y quim* (Madrid) 42, 108-22 (1947).

Another method (Shell Development Co. U. S. Pat. 2,443,063), using a ketone, crystallizes stearic acid up to 99% pure product without refrigeration. Of interest also in the method of separating fatty acids by the formation of thiourea and urea complexes (See J. H. Schlenk & R. T. Holman, J. Am. Chem. Soc. 72:5001-4 (1950) . The only American patent noted relating to this process but confined to hydrocarbon separation is that of L. C. Fetterly (to Shell Devel. Corp.) U. S. Pat. 2,499,320) . These methods do not appear promising as a means of commercial separation of tallow fatty acids.

2A. PROCESSING METHODS TO CHEMICALLY MODIFY FATTY ACIDS

A CARBOXYL MODIFICATION

ESTERS

The general method of preparation consists of direct esterification in the liquid phase using an ester kettle, consisting of an enclosed indirect heated vessel with agitation, mechanical or otherwise, plus a reflux condenser. The water formed is removed by use of air, an inert gas, vacuum, azeotropic distillation with or without a third solvent or combinations of these methods. There is no single method applicable to all types of esters since these vary widely in their solubility, boiling points, stability and other characteristics. Catalysts may be necessary, such as H_3PO_4 , H_2SO_4 , $ZnCl_2$, aryl sulfonic acids, caustic soda, sodium methylate etc. In special cases it is necessary to use other derivatives for the condensation, such as the acid chloride, acid anhydride, etc.

Another method of ester formation is interesterification and more particularly interesterification by alcoholysis. Hansley (U.S. Pat. 2,177,407 (1939) prepares them under pressure. Bradshaw (U.S. Pat. 2,271,619) employs batch methods without pressure. The method consists of converting one ester into another as a fat into the methyl esters.



This important process has been dealt with previously, as a means of preparing fatty acids. Fatty acids from castor oil are commonly prepared this way. Interesterification also includes the exchange of alkyl radicals between two esters, known as ester interchange and between an ester and an acid known as acidolysis.



The more volatile ester is driven off.



In this case the more volatile acid is distilled off.

As a practical example, palm oil containing a high percentage of free acids is treated with a coconut oil. The free palm oil acids are esterified and the liberated lower boiling coconut acids are removed.

The esters differ from the amides and amines in their instability toward acid and alkali and for this reason are most suited to processes and products where they are used under neutral conditions or where they are transitory materials as in foods etc.

To deal with the multiplicity of products available and in present commercial use, it is best to consider the properties of an ester as that of its two constituents - the acid and the alcohol. With such fatty esters as methyl stearate, ethyl palmitate, etc. the properties of the fatty acid far outweigh those of the short chain alcohol. With hexitol monopalmitate, propylene glycol (600) monostearate, etc. the properties of the alcohol may largely transcend that of the acid. With ethylene oxide addition to the fatty acid all grades of transition are available depending on x in the following structure.



The most important class of esters are the triglycerides, previously dealt with under the fats and oils. The next most important class from a commercial production point of view are the polyhydric alcohols including such alcohols as glycerine, the glycols, mannitol, hexitol, sucrose, pentaerythritol, etc. These products are widely used as emulsifiers, in foods and pharmaceuticals. Probable production of such types is estimated to consume 22 million lbs. of animal fats per year of which probably 10 million are monoglycerides of stearic acid for edible, cosmetic and pharmaceutical purposes. This estimate is based on scattered data from producers interviewed, plus Census reports.

The simple esters such as the methyl and ethyl esters of oleic and stearic acids and fat derived azelaic and pelargonic plus miscellaneous cyclic alcohols such as tocopherol (Hoffman La Roche & Co. Brit. Pat. 536,602 (1941) not included above, is estimated at 3 million lbs. of animal fat. This estimate does not include such derivatives as sebacic acid esters widely used as plasticizers, since these acids are largely made from imported castor oil and enters this picture only as a competing material to azelaic.

Oxidation costs of producing azelaic and pelargonic largely determine the extent to which sebacic could be replaced it is believed, although definite information as to the relative merits of these products in comparison with sebacic acid derived products was not forthcoming from the interviews, largely no doubt because the producers of azelaic and pelargonic derivatives themselves did not have the data.

As mentioned above, the properties of the esters are determined largely by the constituent acid and alcohol. For example, the methyl ester of oleic will be modified by whatever additions may be made at the double bond. The epoxy ester of oleic would be such a product. Buffalo Electrochemical Co. for example have been able to make this acid in 84% yield from oleic and peracetic acid. They have investigated the properties of a number of such esters. Cox describes some methyl esters of 12-ketostearate (U.S. Pat. 2,180,730 (1939) and 2,227,823 (1941)). Cyclopentyl esters (Evans et al, U.S. Pat. 2,237,729 (1941)) are useful as plasticizers etc. The α -hydroxy stearic acid would be another. The methyl ester of dichlorostearic acid would be a third. This last compound for example is made by the Hooker Electro-chemical Co. in small amount (probably 25-50,000 lbs. per year) for Continental Oil Refining Co. for use as an additive to lubricants. The pentachlorostearic acid ester is used as a plasticizer. Both products consume about 200,000 lbs. of triple pressed stearic acid a year. Usually the ester of the unsaturated double bonded acid is more stable than the free acid, due possibly to the absence of pro-oxidants in the ester. In the case of the pentaerythritol and dipentaerythritol esters it triggers the activity of the double bond due possibly to the configuration of the ester molecule. Castor and tung oil esters of this alcohol are very fast drying. This last example is by way of illustration only since we are primarily concerned here with tallow, grease and lard and their derivatives. However, in any evaluation of esters the type of products obtained by double bond modification, addition or substitution must be considered as yielding a new product. The possibility of polymerization or other reaction between double bonds of two oleic molecules is another type of modification which would yield interesting di esters. Esterified sulfonated oils are being used as emulsifiers in cutting oils.

The modification of the alcohol portion of the ester must also be considered as giving rise to new types of products. For example polymerizable unsaturated esters such as vinyl esters; substitution products in the alcohol such as sulfonation or sulfation. This last gives rise to an interesting series of fatty derived detergents and wetting agents. Sulfated monoglycerides

(Monad G) which because of their acid and alkali instability (due to the ester linkage), have been entirely replaced in the retail field by the alkyl aryl sulfonates and largely in the industrial field.

The esters find a wide use in a variety of ways in addition to those already mentioned. A few typical patent references bearing on tallow or derived fatty acid esters follow.

- (1) Triethanolamine stearate-for laying dust in mines, roads, etc. U.S. Pat. 2,195,573
- (2) Polyhydric partial esters of fatty acids useful for
 - (a) Preventing crystallization of stearin from salad oils (P & G) U.S. Pat. 2,266,591)
 - (b) As an ingredient of an all synthetic bar soap
(P & G U.S. Pat. 2,356,903)
(Emulsol U.S. Pat. 2,374,213)
(Colgate U.S. Pat. 2,462,758)
 - (c) As a crumb softener for bread. Favor et al, Cereal Chem. 24, 346-55(1947)
- (3) Fatty acid monoglycerides as a defoaming agent for paper stock. (Nat. Oil Prod. U.S. Pat. 2,304,304)
- (4) Butyl oleate, sulfonated.
 - (a) As a textile softening agent.
(Broughton U.S. Pat. 2,325,489)
 - (b) As an ingredient with metal salts to waterproof cement.(Sonneborn U.S. Pat. 2,358,776)
 - (c) To petrolatum (oleate ester)as a pharmaceutical base
(Ninol, U.S. Pat. 2,398,254)
- (5) Short chain esters, where azelaic and pelargonic would probably substitute to some degree.
 - (a) Dioctyladipate - as yarn plasticizer.
- (6) Esters from fatty acid and fatty alcohol, where one contains an hydroxy group, are useful as wax substitutes.
(Snell, U.S. Pat. 2,385,849)

(7) As additives to greases and oils..

- (a) Glycerol monostearate (Emery Ind. U.S.Pat. 2,331,314)
- (b) Oleate ester (Shell U.S.Pat. 2,372,160)
- (c) Chlorosubstituted esters (Commercial U.S.Pat. 2,427,821)
Solvents
- (d) Polymerized esters (Cowan USDA U.S.Pat. 2,384,443)

AN EXAMINATION OF THE ABOVE USES, INDICATES IN A BROAD WAY THE MAIN TYPES OF OUTLETS FOR THESE PRODUCTS. THE LARGEST AT PRESENT IS IN THE MONOGLYCERIDE FIELD. AS IT IS A WIDESPREAD CUSTOM TO PUT EMULSIFIERS IN ALL SHORTENINGS (P & G, MR. BLAIR) IT IS SAFE TO SAY THAT VERY LIKELY 40 to 50 MILLION LBS. PER YEAR OF MONOGLYCERIDES ARE BEING USED FOR THAT PURPOSE. EXCEPT AS ESTIMATED ABOVE IN THIS SECTION, THESE ARE MADE IN SITU AND THEREFORE FROM VEGETABLE OILS OR LARD. THE NEXT MOST INTERESTING USE IS 2c ABOVE. THE RESEARCH ON THIS HAS BEEN CARRIED FORWARD EXTENSIVELY BY ATLAS AND VANDERBILT WHO HANDLE THE EDIBLE PRODUCTS OF ATLAS, AND BY THE MELLON INSTITUTE, RETAINED BY ATLAS FOR INVESTIGATIONS OF THIS NATURE.

ESTERS ARE NOT INTERESTING AS RETAIL DETERGENT PRODUCTS DUE TO (1) A CHANGE IN BUYING HABITS WHICH IS TOWARD THE USE OF BUILT DETERGENTS. SUCH PRODUCTS CANNOT USE ESTERS AS SUCH TYPE PRODUCTS ARE UNSTABLE TO ALKALINE SALTS (2) AND TO TECHNICAL DIFFICULTIES IN SPRAY DRYING WHICH GIVES A HIGH LOSS. IT IS DOUBTFUL IF SULFONATED MONOGLYCERIDES WILL EVER AGAIN BECOME AN IMPORTANT RETAIL PRODUCT. COLGATE ARE NOT USING IT AT ALL AT THE PRESENT TIME IN RETAIL PRODUCTS.

ESTERS SUCH AS POLYOXYETHYLENE DERIVATIVES ARE SUGGESTED FOR RESEARCH AS ADDITIVES TO SOAP AND AS LOW FOAM NONIONIC DETERGENTS, PARTICULARLY SUBSTITUTED STEARIC ACID DERIVATIVES. NO REFERENCES TO WORK OF THIS KIND WAS NOTED.

ESTERS ALSO FORM THE BASE FOR AN INTERESTING STUDY ON PROCESSING. THEY GIVE AN APPARENT STABILITY TO THE DOUBLE BOND DUE POSSIBLY TO THE ABSENCE OF PRO-OXIDANTS. THEY APPARENTLY ARE MORE EASILY DISTILLED THAN THE ACIDS AND MAY BE CONTINUOUSLY (COLGATE U.S. Pat. 2,383,630) OR BATCH (DU PONT U.S. PAT. 2,271,619) ESTERIFIED. RESEARCH ON THE POSSIBLE COMBINATION OF THIS METHOD WITH MODERN METHODS OF SOLVENT CRYSTALLIZATION OR EXTRACTION MAY PROVE VALUABLE, FROM AN EQUIPMENT AND PATENT ANGLE.

CARBOXYL MODIFICATION OF FATTY ACIDS

2. SALTS - A. INORGANIC

(1) Soluble - Potassium, Sodium

The salts of the fatty acids may be roughly divided into two classes (1) The sodium and potassium salts or hard soaps and soft soaps respectively and (2) the heavy metal soaps. The great majority of inedible tallow and grease finds its way to (1). A very much smaller portion, estimated at somewhat less than 100 million lbs. finds its way to use (2). The interviews with petroleum companies in general were negative in regard to specific types of use to which tallow is put, but practically all buy it or its derivatives in car lots to convert principally into such soaps as aluminum stearate, sodium stearate, calcium oleate etc. as an ingredient of a lubricating grease. A very considerable portion of lubricating greases are built with water soluble soaps indicating the overlap of functions among the salts.

Considering first the water soluble Na and K salts which represent by far the largest single outlet for inedible tallow and greases, it is estimated from market data relating to soaps and synthetics, that the latter have displaced some 350 million lbs. of tallow which would have normally gone to that market had synthetics been absent. Furthermore, at the present rate of growth of synthetics, another 30 million lbs. per year of the fats and oil market is being lost, of which about 25 million lbs. represents tallow. This displacement will approach a limit since the synthetics are mainly in competition with soap powders whose total production in 1947 (Census of Mfg.) was 1,522,795,000 lbs. In that year it is estimated that 525,000,000 lbs. of synthetic detergents were sold (all in granular form) making a total consumption of such type cleaners, just over 2.0 billion lbs. Since that time, overall soap sales have remained fairly constant while synthetic for the same period has advanced materially, taking up the slack created by a general increase in usage due chiefly to an increase in population. See the Association of American Soap & Glycerine Producers' data on page 6.

All Companies making synthetics are not members of the above Association and those not members generally produce for industrial consumption. The most recent estimate of total synthetics produced in 1950 is 1.2 billion lbs. which would allow

approximately 900 million as retail package products, in reasonable agreement with the above data, which would place retail consumption of powder detergents at about 2.4 billion lbs. How far synthetics will displace soap is very highly speculative but some consider that it can reach 2.0 billion lbs. (L. F. Flett, Soap & Sanitary Chem. P35, March 1951 and F. D. Snell and C. S. Kimball, Soap & Sanitary Chem. P27, June 1951) which would mean an overall displacement of about 550 million lbs. of fat. These estimates for the most part are based on present commercial applications and uses. There is the category of Toilet bar soaps which could develop a considerable market for synthetics to the displacement of soap, either by the successful formulation of an all synthetic bar or soap plus synthetic bar. The 1947 Census of Manufacturers report placed this soap category at 555,451,000 lbs. which is a considerable potential. This problem is not likely to be solved quickly. One firm for example (Procter & Gamble) has been working on it for over fifteen years.

In investigating research work that is or should be done to increase domestic fat consumption this present large outlet must be given first consideration because of the tonnages involved.

- (1) What research will expand present soap markets?
- (2) What research will expand the use of domestic fats in synthetics?
- (3) Who would be interested in carrying out product application research?

In regard to (1) above, soap is so old that the pattern of its applications has been well established. As long as soap competitors were of minor importance such as the sulfonated oils, etc. there was relatively little need for development work. With synthetics now occupying a large part of the detergent business both retail and industrial, and companies doing planned market research, there is greater need than ever before for market research on soap, to present scientific and unbiased reports to industry and to follow up new product and process development. The following illustrate this.

(1) Lever U.S. Pat. 2,459,818. The use of 5% guanidine stearate in a soap flake to improve its solubility and detergency on soiled dishes.

(2) Procter & Gamble U.S. Pat. 2,263,729. The use of an alkyl phenoxy carboxylic acid salt such as sodium p-octyl phenoxy acetate to increase the solubility and detergency of stearate and hardened whale oil soaps.

(3) The addition of 2% salts of ethylene diaminetetracetic acid to Lux flakes greatly improves hard water stability at 20° C. (Alrose - unpublished report.) The effect falls off rapidly with an increase in temperature. The present use of such sequestering agents in bars is limited due to its leaching out. Such type sequestering agents are rather widely made and patented. Refined Products Corporation,--Permakleer; Bersworth Chemical Company,--Versene; Alrose Chemical Company,--Sequestrene; and General Aniline & Film Corporation,--Nullapon, are examples. Their principle use is to prevent the precipitation of insoluble salts from liquid shampoos and other liquid soap materials. If used in large amounts they could be used to prevent the precipitation of lime soaps when soap is the detergent. However, soap itself is able to sequester its own lime soaps if used in excess. Such addition therefore would have no great value unless the sequesterant could be added to the water prior to its use in the rinse. This appears a rather impractical solution at the moment. However, the sequesterants, as a material for addition to soap, should not be taken lightly and research on these materials should be given careful attention.

(4) The use of amides in soap. Alrose expressed keen interest in this research but gave no indication of its direction or use.

(5) Halogen substitution reactions in the saturated acids (J. B. Williams Co. U.S. Pat. 2,435,828-9) are discussed elsewhere.

The size of the market aimed at here is approximately 400 - 500 million pounds of tallow a year displaced from soap by synthetics. Whatever fraction of this could be recovered would depend on how thorough a job was done by such adjunct, how well the idea was explained and to what extent existing patents could be cross licensed.

Item 2 - Research to Expand the Present Use of Fats in Detergents

INDIVIDUAL DEVELOPMENTS ARE TREATED ELSEWHERE BUT THE RELATIONSHIP OF THEIR IMPORTANCE TO DOMESTIC FAT USAGE IS HERE BROUGHT OUT. IT CAN BE SHOWN FOR EXAMPLE THAT A FAT CONVERTED TO A SYNTHETIC DETERGENT GOES ABOUT 3.5 TIMES AS FAR AS THE SAME FAT CONVERTED TO SOAP. FOR THIS REASON, EVEN IF ALL PRESENT PRODUCTION OF RETAIL SYNTHETIC DETERGENTS ESTIMATED AT 900 MILLION LBS. WERE FAT BASED, NOT OVER 150 MILLION LBS. OF FAT WOULD BE REQUIRED FOR THEIR PRODUCTION OF WHICH NOT MORE THAN 75 MILLION LBS. WOULD BE TALLOW AND THE BALANCE COCONUT OIL. ACTUALLY A LEADING SYNDET (TIDE) IS FAT BASED AND ON DATA OBTAINED FROM PROCTER & GAMBLE, (E.G. THAT TALLOW CAN REPLACE COCONUT OIL UP TO 50%) COULD VERY WELL ACCOUNT FOR A USE OF 25 - 30 MILLION LBS. OF TALLOW. THE PRESENT SIZE OF THIS RETAIL MARKET FOR FAT THEREFORE WOULD BE NOT MORE THAN 60 MILLION LBS. WITH A POSSIBLE INCREASE TO 100 MILLION LBS. IF EXPANSION IN SYNTHETICS CONTINUES UP TO 2 BILLION LBS.. THE DISCUSSION ABOVE IS MADE TO ESTABLISH THE SIZE OF THE MARKET. THE RESEARCH UNDER ITEM 2 ABOVE WILL BE HANDLED UNDER THE SECTIONS DEALING WITH SPECIFIC REACTIONS NOT INVOLVING SOAP.

Item 3 - Who would be Interested in Carrying out such Research?
(Promotion of soap usage as detergents)

Soap producers are at present doing much development work. However, the large producers of soaps already are also making synthetics and therefore have lost, to some degree, the biased point of view they had 10 to 15 years ago. The promotion of synthetics or soaps will vary to some extent as the price relationship of the raw materials. Since synthetics are built on a more stable price structure than fats, the former is bound to be favored in development work.

The small soap companies generally do not have the facilities to do such work. The renderer although vitally interested in the soap picture, since he sells the vast majority of his product to the soap makers, has no individual or coordinated program on this subject. The packer, usually a soap maker also, is probably bearing the brunt of this work. It is the opinion here, based on the interviews, a metamorphosis is taking place in the detergent industry-that tallow as a raw material for soap has lost a large portion of its market and that these facts should be recognized and a coordinated effort made to maintain and extend present uses by a program of market research and development.

(2) Metallic Salts

The variety of heavy metal salts of fatty acids is almost limitless. For practical industrial application they may be classified briefly by their principal salts and use as follows:

1. The paint driers - The cobalt, lead and manganese salts of unsaturated acids such as the linolenates and naphthenates. This class has no interest in this investigation. It is an outlet for vegetable oils.

2. As catalysts for high temperature reactions such as in the oxidation of petroleum hydrocarbons, hydrogenations of organic compounds, as a rubber accelerator for vulcanizing such as Pb oleate, in the manufacture of monoglyceride (Na and Ca soaps of tallow fatty acids) in the reduction of fatty acids by hydrogen, Pb, Cd or Cu salts (Brit. 582,699 and U.S. Pat. 2,340,344, U.S. Pat. 2,365,915 etc.)

3. As dispersing agents and wetters and detergents - To suspend pigments in paints, sludge in lubricating oil etc. These are chiefly the naphthenic acid salts and their formaldehyde condensation products. As a dry cleaning soap - Mg Oleate.

4. For grease manufacture. Generally the stearates, palmitates, oleates or tallow fatty acid derivatives of Na, Al, Ca, Mg, Li and Pb. The mineral oil is considered the lubricating material and the fatty acid soap is the bodying agent which keeps the lubricant in a solid form for easy application, such as in cup greases, etc. The soaps are used for such physical properties as gelling and thickening. There is evidence also that the neutral soaps can actually be lubricants in themselves by the adhesion of the metallic ion to the metal surface of the bearing. This effect is incidental, however. The type of mineral oil used, additives added to the oil, temperature and condition of use, all influence the choice of fatty acid and cation. The sodium and lithium stearates are used at temperatures above 100° C. Ca salts waterproof the lubricant. The petroleum companies, in general, make their own soaps and buy the necessary fats, oils and fatty acids in tank car lots. Certain types of salts require special technique of manufacture and equipment and many companies specialize in supplying the metallic soaps to the trade in various grades - for example Leffingwell, Witco, Metasap Division of National Oil

Products Co. and Hollingshead. The titer of the fatty acid used is important so that normal stearic acid containing 45% stearic and 55% palmitic acid would give one type of grease while hydrogenated tallow fatty acids containing 70% stearic and 30% palmitic would give another type. However, the variables of concentration, choice of metal ion etc. give the manufacturer a choice of conditions so that the availability of fatty acids in a pure state from newer methods of processing (solvent crystallization, fractional distillation etc) is not expected to have much influence on grease manufacturing.

5. The metal soaps also act as thickening and stiffening agents for other materials than lubricants - paints for example. Al stearate is most commonly used followed by Al oleate. Also the thickening of gasoline for use in warfare (Napalm.) Also as solid fuels (U.S. Pat. 1,888,820). Co stearate is used in candles and asphalt as a hardener.

6. As a direct lubricant in

(a) Wire drawing. Zn, Na and Al stearates or the corresponding salts of tallow fatty acids. As simple as it sounds, the type of formula used in wire drawing is quite variable and depends on the type of wire being drawn - such as bronze, copper, steel, iron etc. plus speed of drawing, size of wire and type of dye. For small sizes, the lubricant is usually a solution of common sodium soap. Mr. Miller of the Du Bois Company estimated yearly usage of wire drawing compounds at 18 million lbs.

(b) Surface lubricants for molds, machine parts - Principally the stearates of Ca, Zn, Pb.

(c) Internal lubricant -
In tablets - crayons, pencils to prevent slip - Zn stearate.
In modeling wax, plastics, rubber etc. - Pb oleate.

(d) In extreme pressure (E.P.) lubricants. Pb stearate or oleate.

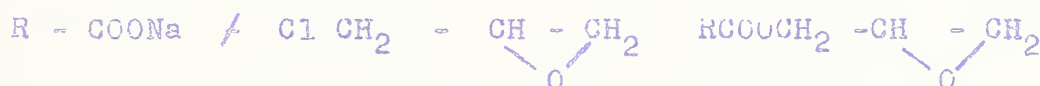
7. As a paint flattener, principally the stearates of Zn, Mg and Ca.

8. As waterproofing agents - The stearates of Al, Ca and Zn and Pb oleate and also where whiteness is a factor. Such uses include coatings on paper, textile, wood and even on the surface of certain chemicals to make them free flowing. Application is made from a solvent. The Zn stearate is of particular interest in textile work.

9. As fungicides and pesticides. The action depends on the hydrolysis of the metal salt and the poisoning effect of the soluble metal salt formed. Hg, Cu and Zn oleate in order of decreasing toxicity as fungicidal sprays, in marine paints, and in salves and ointments. Phenyl mercuric stearate for example is used to prevent mold growth in fat liquoring of leather.

10. Cosmetics and Pharmaceuticals. Zn stearate which may be very finely ground, is white and has mild antiseptic power.

11. Chemical. Pyrolysis of the Ca salts gives the di alkyl ketones and hydrocarbons. This reaction has long been known and to date has had no commercial application. It is not considered important here. A more important use of the heavy metal salts is in alcohol formation. Recent work by both Procter & Gamble (U.S. Pat. 2,340,343-4) and Du Pont (Brit. Pat. 586,799 and 582,699) show that high yields of alcohols are possible by heating the lead, copper or cadmium salts of the fatty acids at temperatures approaching 400° under pressures of hydrogen up to 4000 psi. On a rare occasion the salt of an acid may promote a reaction through its activity. U.S. Pat. 2,448,602 to Kester (Western Regional Research Lab.) uses the sodium salt of a fatty acid and epichlorohydrin to form the glycidyl ester.



Miscellaneous - In mordant dyeing; as an additive to lubricating oil (Cr, Ni, Pb oleates, etc.) and to improve the high temperature resistance of Al stearate greases, by the addition of a small amount of Li stearate (U.S. Pat. 2,431,760.)

Al stearate in 0.1 - 0.5% is added to lubricating oils as a pour point depressant (U.S. Pat. 2,308,116.)

Cr Oleate in 0.25 - 1.0% is added as an anti foaming agent in cutting oils. Ca Stearate as an additive to diesel fuels (U.S. Pat. 2,317,666).

THE MOST INTERESTING INVESTIGATIONS IN THIS FIELD WOULD BE

(1) THE USE OF THE METAL SALTS AS THICKENING AGENTS FOR THE PREPARATION OF SOLID FUELS FOR ROCKET ENGINES ETC.

(2) THE USE OF ADDITIVES TO PETROLEUM OILS IN SMALL AMOUNTS TO INCREASE LUBRICATION. CHLORODERIVATIVES OF FATTY ACIDS, FATTY ACIDS THEMSELVES AND SODIUM ALKYL NAPHTHENATES ARE NOW USED EXTENSIVELY. THE LARGE TONNAGES OF LUBRICANTS INVOLVED MAKE THIS AN ATTRACTIVE FIELD EVEN WHERE ONLY 0.1% - 0.5% ADDITIVE IS INVOLVED. THE MAHOGANY SOAPS, LARGELY A DRUG ON THE MARKET A FEW YEARS AGO, ARE NOW IN GREAT DEMAND, WITH STOCK ALMOST NON-EXISTENT. THE USE OF SMALL AMOUNTS OF PROOXIDANTS FOR USE IN TOP LUBRICATION WOULD APPEAR ATTRACTIVE. THESE REDUCE CARBON FORMATION IN CYLINDER HEADS. AT PRESENT, RESEARCH LEANS TOWARD THE USE OF NAPHTHENATES (GULF OIL CO. U.S. PAT. 2,202,826.) THE STRONGEST COMPETITORS IN THIS FIELD OF METAL SOAPS ARE THE METAL SALTS OF PETROLEUM FATTY ACIDS AND OF THE NAPHTHENATES WHICH LAST HAVE A SUPERIOR SOLVENT SOLUBILITY. IT IS QUITE UNDERSTANDABLE WHY THE PETROLEUM INTERESTS WOULD FAVOR STABLE PRICED MATERIALS OBTAINABLE WITHIN THEIR OWN ORGANIZATIONS. THE ADVANTAGE FATTY ACIDS AND FATS HAVE IS THE CONSTANT COMPOSITION OF EACH PRODUCT SUCH AS SPECIFIC CHAIN LENGTH, KNOWN DOUBLE BOND POSITION, NON-BRANCHED CHAIN ISOMERS, ETC. EVEN SO, THIS MARKET COULD BE LOST THROUGH INADEQUATE RESEARCH PROMOTING THE FAT INTERESTS, OR UNUSUAL AND VARIABLE PRICING CONDITIONS.

2. SALTS - B. ORGANIC

These yield one of the most important industrial outlets for fats, particularly oleic acid as against stearic. It is estimated elsewhere that in 1949 something like 22 million pounds of oleic acid went into chemicals and a good portion of this probably up to 10 million lbs. were first converted to an amine salt and further reacted to a substituted amide. Thus a large part of this production is formed as an intermediate. Such products and the possibilities of such products have been, therefore, part of the discussion on amides. A wide variety of detergent, emulsifying and wetting agents do exist however simply by neutralizing the acid with an organic amino derivative such as monoethanolamine, hydroxyethyl ethylene diamine, guanidine etc. without dehydration. The morpholine soap of oleic used as the emulsifier in water resisting floor waxes must also be excluded since they are transitory compounds formed in situ and therefore purchased not as an emulsifier, but as oleic or other acid for use in a formula.

Ethanolamine soaps are sold chiefly as liquid hand soaps. For this type of use, I see no expansion other than that occurring in the normal business cycle. Use of such products however in synthetic detergents and in regular soaps has been mentioned in the patent literature. Swift & Company (U.S. Pat. 2,483,253) suggest the incorporation of 5-10% in bar soaps to aid texture. Lever Bros. (U.S. Pat. 2,459,818) (Brit. Pat. 581,799) suggest the use of 5% guanidine stearate in soap flakes to improve their solubility, detergency and stability to hard water. Other fat and non-fat derived materials have been mentioned from time to time for purposes of improving soap products. These uses are not to be considered new outlets for fat however, and may actually curtail such, since they replace soap. For example, if 5% of an 82% fatty acid soap is replaced by 5% of an 82% fatty acid ethanolamine stearate, the net change in fat content of the product is zero.

THE CONCLUSION REACHED IS THAT THESE PRODUCTS OFFER NO PRESENT INTEREST IN RESEARCH IN REGARD TO INCREASED TALLOW CONSUMPTION.

3 - AMIDES

The primary amides of the fatty acids are obtained commercially by Armour and Company by passing ammonia through the fatty acids at high temperatures resulting in dehydration of the ammonium salt formed. General Mills is erecting a 30 million lb. per year fatty acid plant at Kankakee for the production of nitriles and no doubt they also will be producers of the amides in the near future. The position appears to be at present, exploratory in this field. Although a large number of types of products are available, it seems to the writer that, as yet, the McCook plant is dependent for tonnage figures on a comparatively few main products such as oleyl amine acetate used in ore flotation. In checking over the methods of preparing amides, it would also appear that the Armour process, while best for preparing pure primary amides, may not be the commercial method used were a special substituted type of amide desired. In particular the ammonolysis of fat (Balaty et al Ind. & Eng. Chem. 31, 280-282 (1939)) deserves close attention as do the other methods briefly discussed below. Compounds of this class are very reactive and unit building blocks of almost infinite variation can be made and are discussed in the patents. In fact, it almost appears that in the rush to patent types and products, their use has been almost lost sight of. Many products are designated as emulsifiers and wetting agents which could only have a limited use in this respect as may be seen by their general structure. As a matter of record, one of the best detergents came out of this group - Igepon T and 702K etc. but its sale in the United States last year did not represent 1% of the synthetics made, chiefly because of its price, being fat based and expensive to manufacture. These cost conditions could alter, of course.

The products of this class as disclosed by the patents, are, in general, waxy solids dispersible in water and showing surface activity. They are made in general without highly complicated apparatus, are far more stable than the ester because of the nitrogen bond and are generally built from a stearic acid base although the other fatty acids work equally as well in many cases. The higher saturated acids require greater care in their preparation than the unsaturated ones. Stearoyl chloride for example condenses very poorly with methyl taurine while oleyl chloride condenses with ease. The ability of this class of compounds to

be built into extremely long and complicated patterns seems to indicate a wider field of use than merely emulsification or wetting, as promising as this field appears at the present time. The vast increase in synthetic fibre production, part of which (nylon) is an amide derivative itself will more and more require special treatment such as creaseproofing, mothproofing, water-proofing, dyeing and filling. Although many of the amide derivatives are now directed toward these uses, particularly as textile softening agents, it appears that a large market awaits development, and the amide (and amine) type compounds present a most interesting field for research. Many of these compounds are reported as high melting point waxes. It is not believed that the amides would be particularly adaptable to use as a wax substitute. The desire in this field (Johnson & Sons) is more for a straight chain acid from C₃₆ - C₅₀, which would lead one to believe that the introduction of internal amide groups are detrimental for this purpose, just as branched chain acids interfere with detergency. In respect to detergency itself, a good deal of research has been done on the amides, particularly by I. G. Farbenindustrie, General Aniline & Film Corporation and by Lever Bros., both here and in Europe. From all types developed to date, the structure is not highly complex. The most complex type evolved probably in the past five years was that of Lever Bros.' BREEZE, the intermediate of which was made by Dow. This has been subsequently changed to an alkyl aryl sulfonate. For these reasons, the probability of an important new detergent emerging from the amides is not promising. This does not exclude possibilities of these materials however as detergent synergists to use in conjunction with soap or other synthetic materials.

The possibilities as ore flotation agents appear quite promising. However, discussion with the research chemists in the metallurgical department of the Battelle Memorial Institute, Columbus, seemed to squash somewhat this idea, irrespective of the fact that Armours main production is directed to this channel of use. The feeling there was that the amides were too expensive as compared with such materials as tall oil even though they were very selective. The tendency in this field is toward using a rough classification with a cheap flotation agent and then to use an amide for the final classification. This procedure would greatly cut down the size of the available market. There are developments in the metallurgical field for the recovery of very low grade materials where this market would be considerable. Their estimate was that this would be an extremely long term project, outside the scope of this report. Mention was made concerning the use of quaternary compounds for non-metallic ore flotation, as mentioned in the patent literature. It was stated

that these type materials were not known to be in use commercially, although admittedly they have been mentioned for this use.

The following very brief outline, indicates to some extent the nature of these products and the type of recent work being carried on by the companies interviewed. Actually, the simple equations below represent only the major reaction. In many cases complex groups of materials are obtained.

Preparation of amides and substituted amides

1. Through dehydration of the ammonium salt

1(a) Above only by producing the ammonium salt in situ from a soap



2. Through dehydration of an organic amine salt.

(Very extensively done under Minol & Carbide & Carbon patents)
Kritchevsky, U. S. Pat. 2,089,212 & Wilson, 2,267,965)

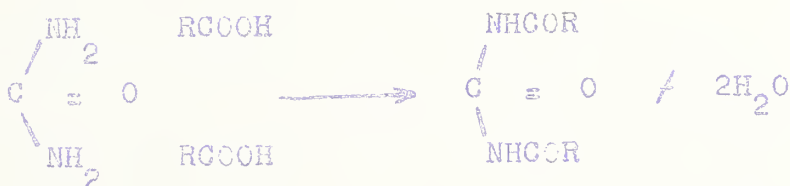
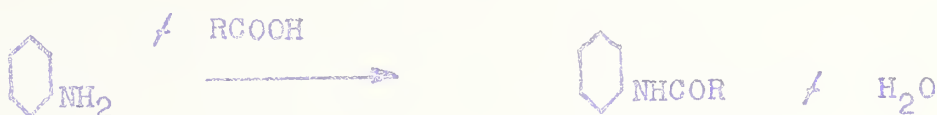


If an ethanolamine is used the free hydroxyl group may be further reacted as with thionyl chloride (Kritchesky U.S. Pat. 2,192,664) or the free hydroxyl group may be displaced by alcoholysis with an ester.
(Shipp, U. S. Pat. 2,232,485)

2 Ethyl palmitate \nearrow ethanolamine \rightarrow palmitoyl aminoethyl palmitate.

Or it may be sulfonated as by chlorination followed by sodium sulfite treatment (Epstein, U.S. Pat. 2,178,139), or added to as with ethylene oxide or paraformaldehyde (Emery Ind. U.S. Pat. 2,393,202.)

3. With aniline or urea.



4. Amine and an acid chloride.

5. Ammonolysis. An ester and ammonia.



Frequently catalysed by alcoholates (U.S. Pat. 2,464,094)

6. Hydrolysis of a nitrile with acid or H_2O_2 .

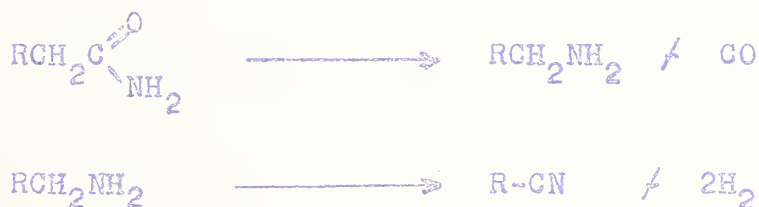


A Few Typical Reactions of the Amide





4. Dehydrogenation.* Amide vapors over reducing Ni catalyst* yield a nitrile plus CO as;



* Mailhke, Bull. Soc. chim (4) 37, 1394 (1925)

5. Substitution as by means of H_2S .



6. Substituted RCONHR'

where $\text{R}' =$

(a) $-\text{CH}_2\text{CH}_2\text{OH}$ - using glyoxal or amides (U.S. Pat's. 2,297,864
U.S. Pat. 2,363,047)

- using formaldehyde in alkali soln.
(U.S. Pat. 2,393,202)

- using ethanolamine on a fatty acid
(U.S. Pat. 2,267,965)

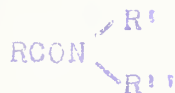
(b) $-(\text{CH}_2\text{CH}_2\text{O})_n \text{CH}_2\text{CH}_2\text{OH}$ with ethylene oxide.

(c) $-\text{SO}_3\text{H}$ - using chlorosulfonic on an amide
Brit. Pat. 506,049 (1939)

(d) $-\text{CH}_2\text{CH}_2\text{OSO}_3\text{Na}$ (U.S. Pat. 2,120,512)

- (9) $-\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$ (either using chloroalkyl sulfonate on an amide with Na in a solvent or using taurine on an acid chloride.)

7.



where $\text{R}' = \text{R} =$

- (a) $-\text{CH}_3$ using dimethyl sulfate (U.S. Pat. 2,329,406)
(b) $-\text{CH}_2\text{CH}_2\text{OH}$ using ethylene oxide (U.S. Pat. 2,266,136)

8. (a) Diamides $\text{R}-\text{CONH}-\text{R}'-\text{NHCOR}$ (U.S. Pat. 2,054,638)
(U.S. Pat. 2,132,388)
(U.S. Pat. 2,329,086)

- (b) Diamides $\text{R}-\text{CON}-\underset{\text{SO}_3\text{H}}{\text{COR}}$ Brit. Pat. 499130.

9. As a base for forming a quaternary, Wirth (Du Pont)
(U.S. Pat. 2,212,654) useful as a waterproofing compound.

The stability of the resulting products in most cases permits many additional reactions to be carried out. For example, the final OH group under 6a may be

- (1) Esterified with an acid anhydride



- (2) Etherified with an alcohol using an acid



- (3) Condensed with urea $\text{R} - \text{CONH} - \text{CH}_2 - \text{NH}$
 $\text{R} - \text{CONH} - \text{CH}_2 - \text{NH}$ (Swiss Pat. 210,976)
 C=O
 NH

(4) Sulfonated.

The R group may be a sulfonated or chlorinated acid. For example the chloro stearamide may be dehalogenated to the sulfonate by means of sodium sulfite according to U.S. Pat. 2,365,431 (1949) to give a wetting agent. See also German Pat. 595,173 (1934).



The above reactions are only indicative of the scope of products available. It is easily seen that polyamino compounds, diamides and such products as urea (U.S. Pat. 2,304,364 Arnold, Hoffman) phthalic anhydride etc. can give rise to polymeric and cyclic structures. Of these the imidazolines are most important from a detergent point of view. The basic patent for the condensation is held by Carbide & Carbon (U.S. Pat. 2,267,965). The only known producer and licensee is the Alrose Chemical Co. at Providence, R.I. but very likely there are a few others such as National Oil Co., at Harrison, N.J. The Richards Chemical Co. has their own process covering these products (U.S. Pat. 2,416,552).

USES OF AMIDES

U.S. Pat. 2,279,314 (Lever Bros.) covers the use of the taurides to impart a slippery feel to detergent solutions. The Emulsol Corporation has a process to make emulsifiers (U.S. Pat. 2,198,806) germicidal emulsifiers (U.S. Pat. 2,388,154) and ore flotation amides (U.S. Pat. 2,302,697), shampoo thickening agents (U.S. Pat. 2,307,047) and the substituted amide from the dehydration of monoethanolamine laurate as an addition agent to bar soap (U.S. Pat. 2,374,213). The National Oil Products Co. has patents covering the use of a diamide as a ceramic lubricant, (U.S. Pat. 2,400,001) and as a rust inhibitor (U.S. Pat. 2,403,293); General Mills (U.S. Pat. 2,461,495) covers polyamides from diamines and malonic acid esters as a coating material; Arnold Hoffman (U.S. Pat. 2,410,738 and 9) as textile softeners, as a plasticizer in resins (Brit. Pat. 567,128).

IN REGARD ALSO TO THE GENERAL UTILITY OF AMIDES CONSIDERATION MUST BE GIVEN TO COMPETING MATERIALS. TALL OIL IS DEFINITELY IN THE PICTURE, BUT ITS TOTAL PRODUCTION IS LIMITED AND ALREADY ABSORBED. SHORT CHAIN AMINES, FROM HYDROCARBON SOURCES AND AROMATIC ANILIDES ARE ALSO STRONG COMPETITORS, AS IS ROSIN. THE VERY REACTIVITY AND COUPLING NATURE OF THE AMIDE GROUP MAKE IT POSSIBLE TO UTILIZE SHORT CHAIN AMINES AND AMIDES TO PRODUCE DESIRED PRODUCTS IN COMPETITION WITH THE FATTY DERIVATIVES. THE GREATEST OUTLETS FOR FATS IN THESE PRODUCTS TO DATE HAS BEEN IN THE FOLLOWING FIELDS.

EMULSIFIERS: MANY INTERESTING TYPES AND WIDE PATENT COVERAGE. COMPETITION STEMS FROM OTHER SHORTER CHAIN AMINO AND AMIDO COMPOUNDS AND FROM FAT AND NON-FAT DERIVED PRODUCTS. SUPERIORITY OF AMIDE TYPE OVER ESTER TYPE IS IN THEIR GREATER ALKALI AND ACID STABILITY BUT THIS IS NOT ENOUGH TO WARRANT A VERY DECIDED PRICE ADVANTAGE IN MANY CASES.

DETERGENTS: CONFINED TO FAT DERIVED IGEPON T EXCLUSIVELY. THIS PRODUCT HAS CONSUMED LESS THAN 1 MILLION LBS. OF FAT IN 1949. THE FACTORS WHICH UP TO THE PRESENT TIME, HAVE LIMITED ITS USE, ARE THE VARIABLE PRICE OF FAT, THE KNOW HOW IN CONNECTION WITH ITS MANUFACTURE AND THE AVAILABILITY OF THE COUPLING AGENT-TAURINE- WHICH LAST IS A DIFFICULT PRODUCT TO PRODUCE. IT IS SLIGHTLY HYGROSCOPIC AND HAS NOT TO DATE BEEN USED IN RETAIL PRODUCTS OF ANY NOTE. THE ALCOHOL SULFATE COSTS LESS TO MANUFACTURE. SINCE THIS PRODUCT AND SIMILAR TYPE PRODUCTS HAVE BEEN KNOWN SINCE 1925 IT IS HIGHLY DOUBTFUL IF RESEARCH WOULD TURN UP ANY NATURAL ACID OR MODIFIED TAURIDE GROUP WHICH HAS NOT BEEN TRIED AND FOUND DEFICIENT IN SOME RESPECT. SUGGESTED RESEARCH WOULD BE ON MODIFIED ACIDS AND IN PARTICULAR ON DEHYDROCHLORINATED MONOCHLORO SUBSTITUTED STEARIC ACID OR PRODUCTS OF SIMILAR NATURE.



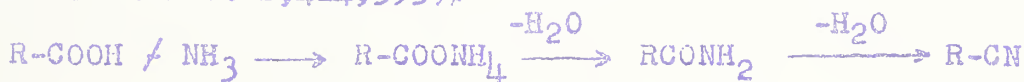
QUATERNARY AMMONIUM SALTS DERIVED THROUGH THE AMIDE HAVE A VERY RAPIDLY AND EXPANDING FIELD OF USE, AS GERMICIDAL AND BACTERICIDAL PRODUCTS. POTENCY IS SO HIGH HOWEVER, THAT EVEN AN OPTIMISTIC FORECAST WOULD HARDLY PREDICT A DIVERSION OF MORE THAN 10 MILLION POUNDS OF FAT FOR THIS PURPOSE. OF 27 COMMERCIAL COMPOUNDS WHERE LENGTH OF ALKYL CHAIN WAS GIVEN, ONLY 6 WERE FROM LONG CHAIN ACIDS INVOLVING OLEIC OR STEARIC, THE BALANCE BEING CETYL, LAURYL OR MYRISTYL. FOR THE PURPOSE OF THIS INVESTIGATION RESEARCH ON ESTABLISHED FATS IN THIS FIELD DOES NOT APPEAR PROMISING.



4 - N I T R I L E S

A number of methods exist for the preparation of the nitriles, most of which are of laboratory interest only due chiefly to the expensive type reagents used, type of raw material etc. A few methods of this class are worthy of further mention. One is the Hofmann degradation where the chain length is shortened one carbon atom. Two, is the reaction of an alkali cyanide with an alkyl halide frequently in the presence of an alcohol, to increase the carbon chain one atom. The latter reaction is the more interesting from a commercial point of view, but even so, there is nothing in the properties of the odd chain nitriles which cannot be duplicated more cheaply and easily from the natural acids.

The prime method of manufacture is, therefore, that occurring through the reaction of ammonia on fatty acids at elevated temperatures in either the liquid or vapor phase. The reaction may be simply explained on the formation of the ammonium soap and its dehydration, first to the amide and then to the nitrile. (I. G. U.S. Pat. 2,177,619), (Emery U.S. Pat. 2,460,772) (Armour U.S. Pat. 2,414,393).



But, from a theoretical point of view, the explanation above is inadequate as it does not take into consideration the fact that pyrolysis of an amide yields equimolecular amounts of both fatty acid and nitrile. See Ralston et al, J. Am. Chem. Soc. 59 986 (1937). That the amide is an intermediate product has been thoroughly established, and in fact forms the chief method of producing this product. The amide itself can be dehydrated to the nitrile by means of various agents such as



carbonyl chloride U. S. Pat. 2,206,351 (1940)
Imperial Chemicals, ZnCl_2 , Al_2O_3

For best nitrile yield, the temperature should be above the decomposition point of the amide. For example, at low temperatures, a fatty acid and urea or cyanuric acid gives the amide



but at higher temperatures and under different conditions (Kaplan U.S. Pat. 2,444,828) the same materials, yield the nitrile. For long chain fatty derivatives this is usually between 400 - 450°C although short chain acids such as sebacic di amide may be dehydrated as low as 250°C. (U.S. Pat. 2,132,849). The removal of the water formed is also an assisting factor. The dehydration catalysts include thoria, alumina, silica gel, aluminum phosphate etc. The vapor phase reaction is illustrated by Nicodemus and Wulff [U. S. Pat. 2,177,619 (1939)] or by Wertz [(Du Pont) U. S. Pat. 2,205,076], the liquid phase by Armour and Co. [Ralston et al. U. S. Pat. 2,061,314 (1936)]. When hydroxy acids are used such as ricinoleic acid, dehydration occurs, and unsaturated nitriles are formed although this is not essential in their preparation since oleic and linoleic will also produce the unsaturated nitriles. [Reutenauer et al Compt rend. 224, 478-9 (1947) and Ind. Corps. gras. 3 174-6 (1947)]. How pure such compounds are made, is not known, although Armour prepares mixed nitriles from tallow, acids and soybean fatty acids. The more unsaturated acids such as linolenic have a tendency to polymerize during the reaction.

Should the demand arise, the nitriles (and amines) of the various fatty acids could be prepared no doubt, in good purity either by using the pure acids to start with or by crystallization means on the mixed nitriles. For economic reasons large tonnage usage will no doubt be largely confined to the use of mixed acids. Tall oil as a potential source of raw material for nitrile manufacturing must not be overlooked either (Armour U.S. Pat. 2,461,349.) The product is a plasticizer for rubber. General Mills who deal chiefly in vegetable and drying oils already have this source of raw material in mind, in all probability.

The fatty nitriles themselves have some use. The C₁₀ to C₁₄ have been mentioned in the literature for use as insect repellents [Ralston, U.S. Pat. 2,280,850 (1942)], as additives to lubricating oils to increase the lubricating qualities [Ralston et al U.S. Pat. 2,053,045 (1936)], as ingredients in penetrating oil [Ralston U.S. Pat. 2,053,046 (1936)], as additives to motor fuels [Conquest U.S. Pat. 2,135,327 (1938)], as ore flotation agents, [Harwood U.S. Pat. 2,166,093 (1939)];

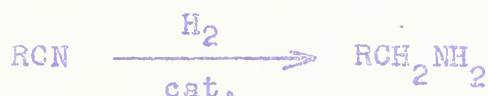
for dinitriles [Gibson et al U.S. Pat. 2,175,093 (1939)] and in soap [Procter & Gamble U.S. Pats. 2,383,525, 2,383,526 and 2,383,737]. The lower molecular weight derivatives have solvent properties. Armour and Company is the only commercial source of these products at the present time. Their capacity is estimated at about 30 million lbs. per year. General Mills has a plant under construction at Kankakee, Michigan for another 30 million lbs. due to be in operation within a few months. The importance of the nitriles lies chiefly in the fact that they are the base for several large classes of products, namely the amines and N-amides, (which last has been previously discussed,) and the quaternary ammonium compounds. Each class, including the nitriles themselves, gives rise to a host of derivatives so that the patent literature is full of references to new compounds the uses of which have to date been only touched on. Although the basic reactions of these materials as discussed above, have been known for many years, some even dating back to the nineteenth century, the commercial availability has been limited almost entirely to the last decade. Indeed, the only present large commercial source of the nitriles (the McCooke plant of Armour & Co.) has only been in operation about a year and a half, although the company has been in pilot plant production for some years at their main Chicago plant.

It can be said therefore, as far as the nitrogen derivatives of the fatty acids in general are concerned, that a rough draft of the course has been plotted, and the basic materials are available in quantity. It remains largely now a matter of exploring the application to industry through market research. This is not meant to infer that continued pure research and applied research is not essential, but merely that a more intensified effort is required at this time on product application. This is reflected in the large number of fat using companies noted who have established special departments for this work under such headings as Research & Development, Product Development, Market Research & Development, etc.

Reactions of Nitriles.

To return to the nitriles, a few important reactions are as follows:

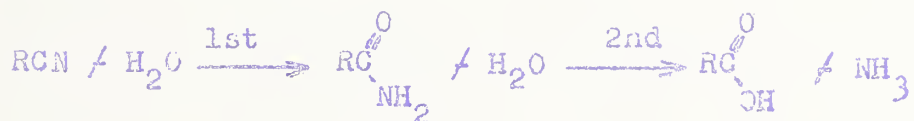
- (1) Hydrogenation to the amine



This reaction is the most important. Yield is improved by addition of dinitriles [Stegemeyer, Emery Ind. U.S. Pat. 2,408,959]. Polymerized dinitriles may also be hydrogenated to polymerized amines (Ralston, U.S. Pat. 2,178,522) and dinitriles having at least 5 C. atoms between the CN groups, to the half amine [Rigby (Du Pont, U.S. Pat. 2,208,598)].

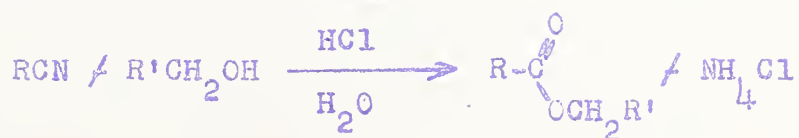
(2) Hydrolysis to the amide and the acid.

This reaction is the least important from the point of view of derivatives, as it merely reverses the method of formation. Its mechanism has importance however, in those cases where the derivative is a nitrile which must be converted to another form for final use, for example, the conversion of the nitrile to a substituted halide derivative followed by hydrolysis to the amide for conversion to a detergent. The mechanism of the reaction indicates that it takes place in two steps - the hydrolysis of the nitrile to the amide and secondly the hydrolysis of the amide to the acid. Under mild acid conditions the second reaction is fast, the first slow, but these rates gradually reverse as the concentration of acid is increased. [Rabinovitch et al. Can. J. Res. 20B 73, 121, 168 and 221 (1942).]



The higher the molecular weight the more difficult the hydrolysis and the more stable the product. Either acid, alkali or steam over a thorium oxide or aluminum oxide catalyst may be employed. Under proper conditions such as by the use of concentrated sulphuric acid, hydrolysis may proceed to the amide only.

(3) Reaction with alcohols



- (4) Thiohydrolysis (Use an alcoholic solution of ammonium sulfide under pressure.)



- (5) Alcohol to imino ether



A phenol may also be used.

- (6) With HCl to an aldehyde



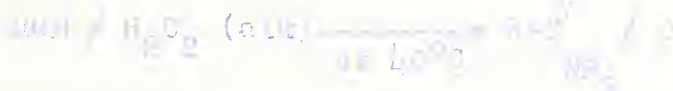
The imino-chloride may be hydrogenated and hydrolysed to the aldehyde although the method is not a good one with the higher fatty nitriles due to low yields [Williams, J.A.C.S. 61 2248 (1939)].

- (7) With Grignard reagents to ketones.

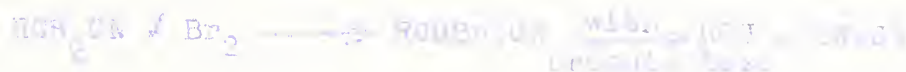


This reaction is of no present commercial value.

(8) With H_2O_2



(9) Halogenation and removal



This product has a double bond and is very reactive as will be typified below. There is no specific information on the higher fatty nitriles but this reaction could be very promising depending on the ease and direction of halogen substitution compared with that of the acid or ester.

(10) Thermal cracking. See Halston patents.

U.S. Pat. 1,991,955-6
U.S. Pat. 2,033,536-7
U.S. Pat. 2,145,802-4

Long chain nitriles are converted to short chain saturated and unsaturated ones, together with hydrocarbons. Since the short chain products are very reactive and in large demand as a base for syntheses this reaction must be considered of prime importance.

(11) With Hydroxylamine to amidoxime



(12) $2RCH_2CN \xrightarrow{Na} RC(NH)CH_2R$

(13) With an acid to a diamide.



(14) With an alkyl iodide



(15) amine to alkyl amide.



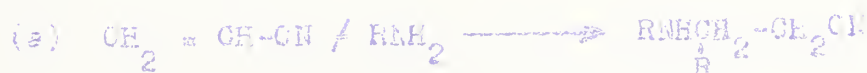
(16) With Ammonia to amidines.



(17) With an ester.



The unsaturated nitriles undergo a wide variety of additions. These unsaturates are available from natural sources such as oleic nitrile, and also from reaction 9 above. For example -





These addition compounds are more interesting from the substituted than the natural unsaturates, because in the substituted product the position of substitution is close to the carboxy or cyano group while in the unsaturates, it is in the middle of the chain. This tends to cut down the effect of the chain length and reduces the general effectiveness to that of cheaper and more available petroleum derivatives. The unique situation about the fatty acids is the long and normal chain lengths. Petroleum sources cannot duplicate this type of compound nor can they duplicate the purity of chain length now available from fats by solvent crystallization and distillation means. Wherever possible, therefore, fat research should favor products and processes where these unique properties are available. Research leading to fission products, consisting of indefinite mixtures should not be favored.

The above reactions are more or less standard for nitriles although a few may be more applicable to the short chain than the long chain compounds. This list by no means attempts to cover all the types but does include those considered important to fat chemistry.

In regard to saturated fatty nitriles, particularly those from stearic and palmitic, the substitution reaction #9 would appear most interesting as a means of increasing their use. In the case of oleic acid, the double bond permits addition reactions such as the formation of dimers and polymers [Ralston U.S. Pat. 2,175,092 (1939)] followed by hydrolysis to poly unsaturated acids [Ralston U.S. Pat. 2,162,971 (1931)] and hydrogenation to polyamines [Ralston U.S. Pat. 2,178,522 (1939)]. With less fundamental change, functional groups may be united according to a few examples listed above (a) to (c) and further exemplified in Markley's Book, Fatty Acids, Interscience Publishers, examples 22-40 pages 504-5. For example oleonitrile reacts with $Hg(OAc)_2$ in ethyl alcohol to yield the 9-acetoxymethyl-10-methoxy stearonitrile useful as a weed killer (Armour U.S. Pat. 2,356,884).

When oleic nitrile is subject to vigorous oxidation fission occurs as in the case of the free acid, yielding pelargonic acid and the semi nitrile of azelaic in small yield (Emery U.S. Pat. 2,468,436)



The esters of these products are useful as plasticizers in various resins (Many U.S. Pat. 2,471,610) such as ethyl cellulose, polyvinyl acetate etc.

THE REACTIONS OF NITRILES ARE CHIEFLY THOSE OF AN INTERMEDIATE, AND AMIDES OR AMIDES AS END PRODUCTS. RESEARCH, THEREFORE, ON THIS TYPE OF COMPOUND WOULD NORMALLY BE DIRECTED AT SHORT CUTS TO REDUCE THE STEPS NECESSARY TO PROVIDE ONE OF THESE SECONDARY DERIVATIVES OR TO STUDY METHODS OF MORE EFFICIENT PRODUCTION. BOTH THESE STEPS WOULD APPEAR SECONDARY IN IMPORTANCE TO WORK ON THE DERIVATIVES. THIS DECISION PARTLY RESTS ON THE FACT THAT OUR PRIME INTEREST LIES IN NITRILES DERIVED FROM PALMITIC, STEARIC OR OLEIC ACID AND NOT FROM THE LOWER OIL NITRILES WHICH MAY IN THEMSELVES HAVE USEFUL PROPERTIES AS INSECT REPELLENTS AND SOLVENTS. EVEN SHOULD SUBSTITUTED DERIVATIVES OF THE HIGHER NITRILES DISPLAY PROPERTIES SIMILAR TO THOSE OF THE LOWER ACIDS, SUCH AS LAURIC OR CAPRIC, IT IS DOUBTFUL IF THE PROSPECTS FOR ECONOMIC ADVANTAGE WOULD WARRANT THE COST OF THE RESEARCH.

5 - AMINES

The amines may be considered a second derivative of fatty acids since they are formed (commercially known as 50%) by the low temperature (Young et al U.S. Pat. 2,287,710 (1942)) hydrogenation of a nitrile which in turn has been derived from a fatty acid by reaction of ammonia at high temperatures.



If hydrogenation proceeds much above 150° (Young et al. op. cit. 2,287,710 (1942)) secondary fatty amines are formed through a complex series of intermediates and which the complexity may be described as follows:



Since ammonia is formed during this reaction, conditions suppressing its formation by such means as adding ammonia under pressure or by using some alkali in aqueous solution (Young et al U.S. Pat. 2,287,710 (1942)) suppress primary amine production, while working the gases (Young U.S. Pat. 2,255,356) and using H₂ catalyst favor primary amine production.

The commercial formation of primary amines, therefore, by catalytic hydrogenation gives rise to secondary amines as an impurity. Similarly, secondary amines will contain primary as an impurity.

The primary saturated and unsaturated amines may also be formed from nitriles without secondary amine formation by the sodium reduction method where sodium is dispensed in toluene etc. (Harwood, U.S. Pat. 2,194,340 (1939)) and by many other methods which at the moment appear to have remote commercial importance.

as far as fatty acid derivatives are concerned due to the type of raw materials required and the costs involved in manufacture. In many of the lower amines this restriction would not occur and materials such as halides, aldehydes, esters and alcohols are available. A few of these are

- (1) The reaction of NH_3 on an alkyl halide



I.G. Ger. Pat. 648,088

- (2) The addition of NH_3 to an alcohol at high temperatures (350°) in the presence of a dehydrating catalyst.



U. S. Pat. 2,078,922 (1937)

- (3) The hydrogenation of aldehydes and ketones

Reppe	U.S. Pat. 1,762,742 (1930)
Vanderbilt	U.S. Pat. 2,219,879 (1940)
Olin et al	U.S. Pat. 2,278,372-3 (1942)
Olin et al	U.S. Pat. 2,367,366 (1945)

- (4) By hydrogenation of an amide at high pressures over Cu and Cr oxide catalysts. [Rohm & Haas Brit. 425,927 (1935), Adkin U.S. Pat. 2,143,751 (1939).]

The formation of primary amines from non-fat sources has some interest. Armour & Co. now produce such amines from rosin concentrated tall oil. Short-chain amines have been prepared from nitroparaffins. Chlorinated paraffins can be converted to amines with ammonia [Profft U.S. Pat. 2,305,830 (1942)]. As with all hydrocarbons however, the product formed would have the

475 FIFTH AVENUE NEW YORK 17, N. Y.

disadvantage over fatty derived products in the uncertainty of composition, difficulties of separating isomers and the presence of branched chains. About 90% of the replies reported that there was no immediate concern over the Fischer-Tropsch and Oxo process as a source of fatty material. I am not inclined to accept this completely, as reliable, however. As of now, or in the next five years, there appears little to warrant concern. On a long term basis there is, and it is felt that the fat industry should be made aware of the danger involved in complacency, and unstable fat price. Sun Oil is already finding short-chain synthetic acids superior to stearic acid in grease manufacture. Synthetic fatty acids are bound to be favored by the petroleum industry over natural fats. Patents covering short-chain acid derivatives also specify Oxo derived products as suitable and recently Du Pont [Brit. Pat. 605,848 (1948)] have synthesized long-chain acids using a short-chain acid ethylene and a benzoyl peroxide catalyst. For example:



The product had an acid value of 75.8 and an average mol. wt. of 740 corresponding to an n of about 24 or chain length of 51 carbon atoms. Conditions of the experiment were 70-82° at 895-950 atm. with a pressure drop of 55 atm. after 18 hours. Considering ethylene at 2¢ per lb. and acetic acid at 10¢ the ingredient cost of this operation would be just under 4¢ per lb. for a C₁₈ fatty acid or under 3¢ for a C₃₆ product. This excludes 18 losses, operation, equipment, 36 profits, etc. Even so, it appears to the writer, that if any incentive were needed by the fat industry for a concerted effort on research, this patent would provide it.

Secondary amines can be made, as mentioned above, by high temperature addition of NH₃ to the nitrile, by hydrogenation of amides at 260 - 280° over copper-chromium oxide catalyst with [Brit. 425,927 (1935)] or without [Adkin U.S. Pat. 2,143,751 (1939)] solvents, and from alcohols and low molecular weight amines (Smeykal, U.S. Pat. 2,043,965 (1936))



No attempt is made here to depict the mechanism of the reaction. Secondary amines can also be made from primary amines by means of formaldehyde and formic acid [Kirby U.S. Pat. 2,356,531 (1935)]



Tertiary amines may be formed in general from a secondary amine and an alkyl halide in liquid ammonia.

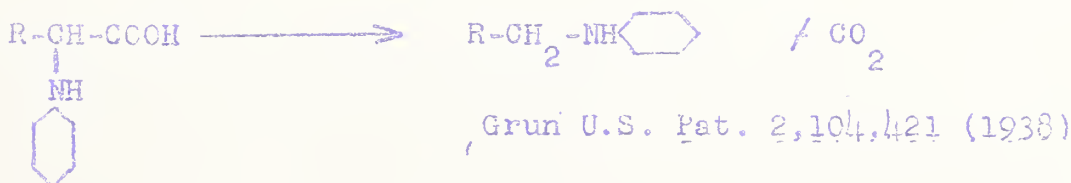


or from a secondary amine and a primary alcohol



Or by reacting formaldehyde and formic acid on a secondary amine as given above.

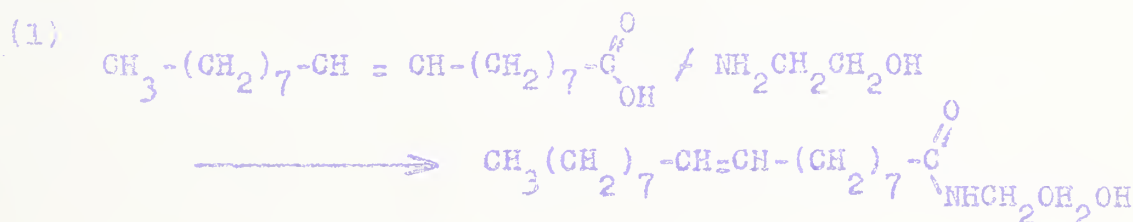
Attention must be drawn to a few special types of products to which the general methods above are applicable. For example, the dinitriles and polynitriles mentioned in the previous section can be converted to the di- and polyamines by methods similar to those used for mononitriles. Decarboxylation of substituted acids gives secondary amides, etc.



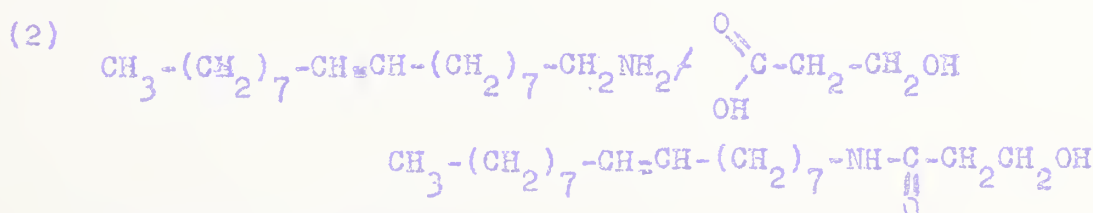
A STUDY OF THESE PROCESSES DOES NOT INDICATE A METHOD OF FORMATION OF COMMERCIAL IMPORTANCE OTHER THAN THOSE NOW EMPLOYED, NAMELY BY THE HYDROGENATION OF NITRILES. ANY OTHER PROCEDURE INVOLVES THE FORMATION OF STEARYL ALCOHOL, OR HALIDE, ETC. WHICH OPERATIONS WHILE FEASIBLE, ARE EXPENSIVE IN THEMSELVES AND NOT COMMERCIALY FEASIBLE BY METHODS NOW KNOWN.

Reactions of the Amines

This is an important type of derivative although the commercial uses have not been developed to a high point. As far as fat consumption is concerned, the non-fat amines have considerably more importance than the fatty ones, as they are used to form stable amides by dehydration of the salt as discussed under the section on amides. Using a fatty amide would decrease water solubility to a point where the product would be suitable only in solvents, while using a fatty amine to condense with a short-chain organic acid would add an unwarranted expense. For illustration only



Normal procedure



Abnormal procedure.

Practically all present production of commercial substituted amide detergents and emulsifiers are made as per equation 1 above. The chief exception is Igepon T where the acid chloride instead of the acid itself is used to condense with a substituted sulfonated amine.

The importance of the fatty amines does not lie in their potential use as detergent bases or emulsifiers but rather in the fact that they are cationic type products which are substantive to fibers. They find their greatest use as substantive materials for fabrics where they can impart hand, creaseproofing, waterproofing, flameproofing, and other desirable characteristics. Because of the stability of the products and their versatile reactions they could become very important in plastics, paper, textiles and metal treating compounds. It is doubted here that they could form the base of an effective detergent, even in the face of many patents to the contrary. Investigation to date on detergency favors the nonionic or anionic type product.

The ready salt formation of the amines with their ready dehydration to amides at temperatures close to the boiling point of water, formation of complex metal salts, of hydrates and eutectics and polymorphic forms renders these compounds particularly reactive.

The most interesting reaction is the addition of ethylene oxide. This process is now commercially developed to a point where practically all large and a few small companies are employing it. It is a powerful, relatively new, cheap tool for modifying the water solubility characteristics of long-chain organic derivatives in the emulsification and detergent field. Atlas Powder Co., Hercules Powder Co., Glyco Products, General Aniline, Monsanto Chemical Co., Wyandotte Chemical Co., Rohm & Haas and Armour and Co. are a few such companies. The addition takes place readily with the OH or NH₂ groups and Armour, the last company named, has a series of such compounds covering all their main derivatives-fats, amides and amines. For purposes of comparison (although given elsewhere also) a few types follow:



(b) Alkyl Phenol



(c) Alcohol



(d) Amide



(e) Amine



(See Ralston U.S. Pat. 2,229,307)

It is this last reaction with which we are concerned here. Probably the first few moles of addition are on one "H" but above 4 or 5 moles, (Armour's information) both H's are substituted as shown.

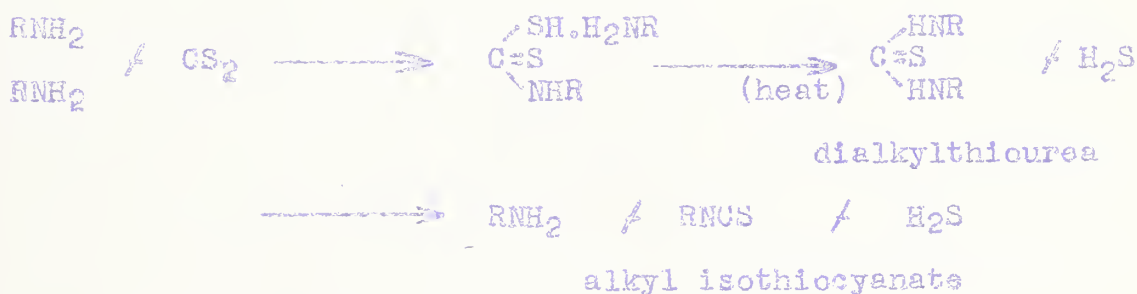
The polymerization of the ethylene oxide by itself is possible, and is sold as "Carbowax" by Carbide and Carbon Chemical Co. Some smaller companies, not equipped for use of ethylene oxide itself, which is somewhat hazardous, use such products quite freely in esterification processes. Alrose Chemical Co., Kessler Chemical and formerly (4 or 5 years ago) Glyco Products.

As far as known, only Armour use ethylene oxide for amine and amide condensation (their Ethomeens and Ethomids). The Ethomeens are cationic in varying degrees becoming more non-ionic as the moles of ethylene oxide increase. Since detergency requires the material to be in a colloidal state, increased water solubility through the addition of too many moles of ethylene oxide can have an adverse effect. Stearylamine has its best

surface tension with 5 moles of ethylene oxide, best wetting time with 10 moles (See Ethoxene, Ethonids & Ethofats, Armour & Co., 1949.)

Ethylene oxide has three very valuable properties when used in conjunction with fats - it makes it possible to modify water solubility (and coincidentally oil solubility), it leaves a terminal hydroxyl group which may be further reacted, and it can increase the solidifying or melting point since the high polymers are waxy solids. Its fourth property - decrease in water solubility with temperature increase may or may not be valuable depending on use. Usually this is considered a drawback, chiefly because it reverses the normal thinking on the subject. My opinion (based on the survey) is that this property is a most valuable one. It should eventually be possible to tailor a compound whose colloidal solubility would remain constant under a wide range of temperature.

2. CO_2 & CS_2 act as coupling agents, giving rise to carbamates, thiocarbamates, dialkyl ureas and alkyl isothiocyanates, etc



3. Heat with a dehydrating catalyst such as ZnCl_2 [Green U.S. Pat. 2,101,314 (1937)] or H_3PO_4 [McCorkle U.S. Pat. 2,355,314 (1944)] leads largely to olefins. These reactions are not interesting commercially.

4. Other reactions include

- (a) Sulfonation, I.G. Brit. 512,022 (1939)
Zerweck et al U.S. Pat. 2,086,690 (1937)
- (b) Oxidation, Engelmann U.S. Pat. 2,159,967 (1939)
- (c) Metallic nitrile formation as $(\text{C}_{10}\text{H}_{21}\text{NH}_3)_3\text{CO}(\text{NO}_2)_6$

[Goebel et al U.S. Pat. 2,274,058 (1942)] and many other
metallic salts Ralston et al, J. Am. Chem. Soc. 68
67 (1946) some useful as rust inhibitors.

- (d) (Additions to unsaturated esters (General Mills
U.S. Pat. 2,468,012)



An infinite variety of further reactions could be
mentioned where the amine group (or amide) can be coupled with
other building blocks, as for example with a chlorohydrin
[Ralston U.S. Pat. 2,229,307 (1941)] nicotinic acid (Katzman
Emulsol U.S. Pat. 2,304,330) and the chloroacetamide of mono-
ethanolamine (Katzman to Emulsol Corp. U.S. Pat. 2,328,021.)

Several comments seem pertinent at this point in
regard to derivatives in general and the amines in particular.
First, only one company is making the higher fatty amines on a
commercial basis. Being pioneers in this field they have built
up over the past 10-15 years a well rounded patent structure
covering processes, products and uses and have published a great
deal of general information on the physical and chemical character-
istics designed to interest other research workers and to extend
the market possibilities of their products. They have built a
subway so to speak into the suburbs. There is no question that
they built this line because they thought there were enough people
at the end to make it pay. But now the line is in, there is bound
to be a rush to buy property. Armour, has pioneered the develop-
ment on fatty derivatives and certain basic uses have been found
in sufficient tonnages to keep a large plant operating. They have
probably built their line into a pretty thinly populated area.

Principal uses of fatty amines and amine salts to date.

- (1) Non-metallic ore flotation as calcium phosphate and
carbonates from silica (Kirby of Du Pont U.S. Pat.
2,221,485) KCl from NaCl etc. [Lenher U.S. Pat.
2,132,902 (1938), Tartaron U.S. Pat. 2,222,728 (1940),
Kirby U.S. Pat. 2,088,325 (1937) & Ralston U.S. Pat.
2,298,281 (1942) 2,313,360 (1943)]

- (2) Bactericides - Ralston U.S. Pat. 2,247,711
- (3) Emulsifier - Dohse et al U.S. Pat. 2,191,295 (1940)
- (4) Waterproofing cement etc. Ralston et al
U.S. Pat. 2,317,301 (1943)
I.G. Brit. 467,166 (1937)
- (5) Insect repellent - Ralston et al Oil & Soap 18, 11(1941)
- (6) Dyeing - Fr. Pats. 782,802 (1935) & 783,008 (1935)
- (7) In enamels, lime etc. Hovey U.S. Pat. 2,230,326 (1941)
and Ralston et al U.S. Pat. 2,320,009-10(1943)
- (8) Water clarification - Ralston & Pool U.S. Pat. 2,315,734
(1943)
- (9) Rust inhibitor in lubricating oils - Gulf Oil
U.S. Pat. 2,387,537 in Diesel fuel, Gulf Oil
U.S. Pat. 2,433,243).

The short chain amines are still basic building blocks and it will probably be some time before the C_{12} - C_{18} chains are able to be used in the same manner that the C_4 and C_6 are being used at present. I believe as a consultant, and with some basis of opinion from the survey, that large tonnage use of the amines will only be developed when these are used as units in far more complicated products than have been developed to-date where their definite and long-chain structure will prove superior to petroleum derivatives.

For the same reasoning as above, the secondary symmetrical long-chain amines are less interesting than the primary, and the tertiary less than the secondary. This does not include the unsymmetrical tertiary amines used extensively as textile softening agents or the unsymmetrical quaternary ammonium compounds widely made and used not only as textile softening agents but for waterproofing as well.

Rohm & Haas (U.S. Pat. 2,209,383), Warwick Chemical Co. (Brit. 560,448), du Pont (U.S. Pat. 2,402,526).

The actual tonnages of material of this nature is small, estimated at 4-5 million lbs. and the possibilities for expansion are good. For example, just within the past year a large petroleum Company (Oronite Chemical - a subsidiary of Standard Oil of California) has entered this field in competition with such companies as Winthrop-Stearns, Fairfield Laboratories, Alrose Chemical Company, Armour and Company, Onyx Oil and Chemical Company, Du Pont, Fine Organics, Rohm & Haas, Nopco Chemical etc. These compounds are based principally on the lauryl alkyl chain and are therefore of little interest as far as tallow is concerned. They contain somewhat less than 50% fat derived product.

THE AMINES AND AMIDES FORM THE MOST INTERESTING CLASS OF FAT DERIVATIVES BECAUSE OF THE MANY TYPES OF REACTIONS POSSIBLE. THE SHORT NON-FATTY AMINES ARE COMPETITORS TO THOSE WHICH ARE FAT DERIVED AND IN MANY CASES THE FATTY ALKYL PORTION OF THE MOLECULES IS PRESENT IN MINOR PROPORTION. ALTHOUGH RESEARCH IN SUCH A DIVERSE FIELD IS BOUND TO BE PRODUCTIVE OF NEW PRODUCTS AND USES, IT IS THE OPINION HERE, THAT SUCH USES WOULD LARGELY BE SPECIALIZED PRODUCTS HAVING SMALL TO MODERATE TONNAGE VOLUME, WHICH IN TOTAL COULD ASSUME A FAIRLY LARGE TONNAGE. THIS OPINION IS BASED ON AN EXAMINATION OF THE PATENT STRUCTURE IN THIS FIELD PLUS THE OPINIONS EXPRESSED IN THE COURSE OF THIS SURVEY.

ONE CAN NEVER TELL HOWEVER, WHEN A SINGLE PRODUCT OR TYPE PRODUCT WILL BLOSSOM INTO AN UNPREDICTED USE OF LARGE VOLUME. THE AMINE SALTS IN REGARD TO ORE FLOTATION IS JUST SUCH A CASE. ITS PRESENT RATE OF CONSUMPTION IN THIS FIELD FOR FAT DERIVED AMINES IS ESTIMATED AT OVER 150,000 LBS. PER YEAR WITH A POTENTIAL USAGE OF 4 TO 5 MILLION LBS. PER YEAR.

IT IS SUGGESTED THAT RESEARCH IN THIS INTERESTING FIELD BE APPROACHED FROM A DIFFERENT VIEWPOINT THAN APPEARS TO HAVE BEEN THE CASE. IN ORDER TO ESTABLISH THE PRODUCT BEYOND THE REACH OF COMPETITIVE MATERIALS, THE PRODUCT MUST UTILIZE THE NATURAL PROPERTIES OF THE BASE UNITS TO THE GREATEST EXTENT. IN THE CASE OF THE FATTY AMINES, (AND AMIDES, SINCE THE DERIVATIVES OVERLAP) THESE SEEM TO BE TWO FOLD.

- (1) THE NORMAL FATTY CHAIN WILL ADD WATER INSOLUBILITY, RESILIENCE AND PLASTIC QUALITIES TO A PRODUCT.
- (2) THE PRODUCTS ARE, OR CAN BE MADE CATIONIC.

IN CASE 1, INVESTIGATION WOULD PROCEED ALONG THE LINES OF MAKING THE FATTY RADICLE A CHEMICAL ADDITION PRODUCT TO OTHER PRODUCTS USED IN LARGE TONNAGE. FOR EXAMPLE PLASTICS, SYNTHETIC TEXTILE FIBERS, CELLULOSE, AND PAINTS. THE STRENGTH OF THE N BOND WOULD MAKE SUCH BUILT IN RADICLES SUPERIOR TO THE ESTER GROUP ALTHOUGH IT IS QUITE CONCEIVABLE THAT THE ESTER COUPLING WOULD BE DESIRABLE ON OCCASION FOR THIS VERY PROPERTY. SOME WORK ALONG THESE LINES HAS BEEN DONE, BUT HAS TO DATE NOT BEEN VERY FRUITFUL.

THE PRODUCT CAN BE MADE SUBSTANTIVE TO MANY FIBERS OR SURFACES. THIS PROPERTY OF THE QUATERNARY DERIVATIVES HAS BEEN THE ONE MOST EXTENSIVELY EXPLOITED TO DATE IN TEXTILE APPLICATION.

TO CONCLUDE THEREFORE, IT APPEARS THAT A PROMISING FIELD FOR RESEARCH IS AVAILABLE FOR FATTY DERIVATIVES WHICH THE EDISONIAN APPROACH TO DATE HAS NOT UNCOVERED.

6 - ALCOHOLS

These are commercially available from Du Pont. The other large producer is Procter & Gamble who manufacture for their own use, converting the product to sulfates for incorporation into TIDE, PRELL and DRENE. It is believed that a small part is used also in DREPT. TIDE is the largest selling synthetic detergent in America and it is estimated between 50 and 60 million pounds of fat a year are consumed in its manufacture. Prior to the advent of TIDE about 1946, alcohol derived synthetic detergents were being made exclusively from coconut oil. Recently an increasing amount of tallow has been used. Mr. Blair of Procter & Gamble considered that tallow might be substituted up to 50% for coconut oil fatty acids. Through other channels (Lever Bros.) analysis indicates considerable amounts of tallow fatty acids are present. On a basis of a 50/50 split, approximately 25 to 30 million lbs. of tallow would be converted to alcohols for sulfation in 1949. To this add 10 million for industrial uses, including those made by Du Pont and an estimated 35 to 40 million pounds are produced. Total fats going to produce alcohols from all sources then is estimated at approximately 70 million pounds.

Many patents have been taken out on methods of production but briefly three commercial methods are in use.

- (1) The sodium reduction method, owned by Du Pont, [Scott & Hansley, U.S. Patent 2,019,022 (1935). For description see Hansley, Ind. & Eng. Chem. 39, 55-62 (1947)] and licensed by them to Procter & Gamble, operates on the glycerides and the glycerine is recoverable.



Yield is about 87%. 57 lbs. of sodium is required per 100 lbs. of lauryl alcohol made, which is 115% of the theoretical amount required by the above equation.

- (2) Strange as it may seem Du Ponts themselves use high pressure hydrogenation over a copper chromium oxide catalyst to effect this conversion. The glycerine is destroyed.
- (3) A third commercial method is the high pressure hydrogenation of the fatty acids used by Procter & Gamble at their Long Beach plant. This process was installed with the purpose of making at least a part of Procter & Gamble's alcohol production independent of sodium. This latter, until recently was available from Du Pont only. Both Procter & Gamble and Du Pont have recently become interested in the high pressure (4000 psi) reduction of the heavy metal salts (Procter & Gamble U.S. Pat. 2,340,343-4, Brit. Pats. 584,939 & 585,219, Du Pont-Brit. Pats. 582,699 & 586,799). Temperatures range from 240 up to 400° without excess hydrocarbon formation. The interest displayed by the two leading producers should warrant close attention to this method.

A number of laboratory methods also exist. A recent one (W. G. Brown, J.A.C.S. 69 2548-9 (1947) uses lithium aluminum hydride (LiAlH_4).

The most important product of the alcohols is their acid sulfate ester - formed when concentrated sulphuric or preferably chlorosulfonic acid is reacted with the alcohol under slight pressure (Procter & Gamble U.S. Pat. 2,231,979, U.S. Pat. 2,214,254, U.S. Pat. 2,187,244; Colgate U.S. Pat. 2,235,098 & U.S. Pat. 2,235,534)



Neutralized acid ester forms the basis for the bulk of the production. Generally the Na salt is used, except for the organic salts such as the triethanolamine salt for high lathering shampoo base materials. Industrial products are sometimes neutralized with K and NH_4 . Other reactions include the formation of dialkyl sulfates as by the conversion of the alcohol to an alcoholate and reacting this with an alkyl chlorosulfonate, Levaillant Compt. rend. 188, 261(1929); the formation of phosphoric acid esters, useful as plasticizers (Granes U.S. Pat. 2,005,619 (1935); the decomposition of an alcohol to an olefine through dehydration at elevated temperatures in the presence of an activated aluminum oxide or similar dehydrating catalyst, Egloff et al J. Am. Chem. Soc. 61, 3571 (1939)]



and the dehydrogenation of an alcohol at elevated temperatures in the presence of a metallic catalyst such as Ni or Cu so yield a heterogeneous mixture of olefines and some aldehydes [Herndon et al J. Am. Chem. Soc. 50, 3066 (1928)]



Of more interest is the following reaction where the alcohol gives up its hydrogen to an olefine and is itself converted into an aldehyde Lyubarskii J. Applied Chem. U.S.S.R. 5, 1025-45 (1932)



Ethylene oxide adds to alcohols to produce emulsifiers having considerable use in industry. Brij for example is an Atlas oil in water emulsifier for non-food use. The product is an ethylene oxide condensate of lauryl alcohol.

Uses other than as detergents may be listed as follows:

- (1) Sulfoacetic acid ester of ^(a)lauryl alcohol, [Harris, Emulsol, U.S. Pat. 2,221,377] as a wetting and anti spattering agent.
- (b) Octyl alcohol - [U.S. Pat. 2,190,921] anti. spattering agent and for ore flotation.
- (2) Oleyl alcohol and short unsaturated acid, as an additive to mineral oils (Petrolite Corp. U.S. Pat. 2,384,595)
- (3) Oleyl phthalate as an anti gumming agent in oils (Socony-Vacuum U.S. Pat. 2,388,400)
- (4) Oleyl alcohol - air blown for textile use, [National Oil Products Co. U.S. Pat. 2,200,298 and U.S. Pat. 2,203,641-2]
- (5) Fatty alcohol sulphates in soap (Colgate U.S. Pat. 2,289,044)

THE USE OF THE HEAVY METAL SALTS FOR ALCOHOL PRODUCTION BY BOTH PROCTER & GAMBLE AND DU PONT IS VERY INTERESTING AND SHOULD BE WATCHED. FURTHER EXPANSION OF TALLOW INTO THE SYNTHETIC DETERGENT FIELD TO REPLACE AN ADDITIONAL 25 MILLION POUNDS OF COCONUT OIL IS A POSSIBILITY, IF A SATISFACTORY SUBSTITUTED STEARIC COULD BE OBTAINED. THE ALCOHOL SULFATE DETERGENTS ARE EXCELLENT AND PRICE ALONE COMPARED TO THE ALKYL ARYL SULFONATES IS THE DRAWBACK. IT IS ESTIMATED THAT 13¢ ARYL SULFONATE (40% ACTIVE) IS EQUIVALENT IN VALUE TO THE ALCOHOL SULFATE WHEN THE LATTER IS PRODUCED FROM 7¢ RAW MATERIALS.

COMMENTING ON LEVER'S SWITCH TO THE MAGNESIUM SALT OF THE ALKYL ARYL SULFONATE, PROCTER & GAMBLE SAID THEY WERE WATCHING THIS DEVELOPMENT WITH INTEREST. THE USE OF ETHYLENE OXIDE AS A SOLUBILIZING AGENT FOR STEARIC ACID SHOULD BEAR FURTHER INVESTIGATION.

7 - MISCELLANEOUS CARBOXYL MODIFIED DERIVATIVES

The aliphatic chlorides, anhydrides, aldehydes, ketones, ethers, sulfides, mercaptans are relatively unimportant commercially, although a great many laboratory reactions are described. The chloride is used for special type condensations, its preparation is generally made with PCl_3 and washing out the phosphorous acid. Long chain ketones can be made by heating the calcium salts of the soaps.



The product seems to have little use. Socony-Vacuum (Meyer et al U.S. Pat. 2,410,096) prepares the unsaturated ketone from a fatty acid at $300 - 350^\circ$ in the presence of a reduced iron catalyst. Colgate (U.S. Pat. 2,321,020) reduces the ketone to a secondary alcohol and sulfates it to a wetting agent.

2 - Processing Method to Chemically Modify Fatty Acids.

(B) INTERNAL CHAIN MODIFICATION

(1) ELAIDINIZATION, double bond shift reactions, conjugation etc. are unimportant commercially at the present time in regard to animal fats. Double bond shifts are extremely important in drying oils however. The conjugation of soybean oil and its esters and acids is of some importance to tallow inasmuch as it diverts part of its production from the edible field and possibly leaves more room for edible animal fat products. Except for mentioning this, it is considered too oblique an approach for further study here.

(2) ADDITION REACTIONS

Addition reactions are important in the chemistry of oils. The most important and common is the addition of hydrogen to the double bond of oleic acid. This reaction is carried out in the presence of a catalyst and under moderate pressures. Since oils do not require such high resisting material, do not require the catalyst and reduce under normal pressures, it is common practice to hydrogenate the oils only in special cases where the oil is not available, as in the case of tall oil or oxidized seed stocks.

Halogen addition to the acids is of more theoretical than practical interest. The dehydrochlorination of oleic for example gives a mixture of conjugated and non-conjugated acids whose pentaerythritol esters are suitable as drying oils. However this could never compete against naturally occurring acids or the conjugation process for linoleic glycerides or esters.

The double bond of oleic acid is an important opening in the molecule for the addition of many modifying groups such as a phenyl by means of a Friedel-Crafts catalyst (Stirton et al J. Am. Oil Chem. Soc. 25 365-8 (1948); a sulfate or sulfonate widely used on ester derivatives of oleic to increase wetting power and hydroxy groups added by means of partial oxidation. The double bond in oleic acid provides a ready means of making a complete new series of substituted stearic acids, such as the hydroxystearic and epoxystearic acids by H_2O_2 oxidation, (General Mills U.S. Pat. 2,452,484) which are useful as plasticizers, solvents and intermediates etc. Oleic with H_2O_2 and formic acid gives the hydroxyformoxy derivative which hydrolyzes with alkali to the dihydroxystearic (Swern et al J. Am. Chem. Soc. 67, 1786-9 (1945)).

(3) FISSION -A. UNSATURATED ACIDS - OLEIC

Fission products are among the most interesting oleic acid derivatives, as they generally lead to two products which have considerable use - pelargonic acid, very useful as a plasticizer in vinyl resins when esterified, and azelaic acid which displays many of the reactions and uses of adipic and sebacic acids. Polymethylene diamine derivative of azelaic acid has fibre possibilities with diimides (Coffman et al, Di Pont, J. Polymer Sc. 2,306-13 (1947)). The esters of these derivatives are useful in grease (Rohm & Haas U.S. Pat. 2,429,934).

The commercial method presently being used by Emery (Pitzpatrick et al. U.S. Pats. 2,389,191 & 2,450,858) to clean oleic acid, is dichromate oxidation with subsequent regeneration of the spent chromium sulphate by electrolysis. The H_2 generator is used to harden more stock. The yield of products ² is believed to be approximately 80%. Emery are not satisfied with this method and are taking steps to put a new one into effect, details of which are not available at this time.

HNO_3 has been mentioned (National Oil Products U.S. Patent ³ 2,365,290) as an oxidation reagent but it is too drastic and gives too many side reactions. $KMnO_4$ is too expensive. Air oxidation is probably the most interesting ⁴ and has the greatest commercial possibility of success. Work on this is proceeding at both the Eastern and Northern Regional Research laboratories. The fission does not proceed as one might normally expect nor are high yields of fission products obtained by present techniques due to the formation of by-product polymers. Hydroperoxides are first formed with fission occurring on either side of the 9 - 10 bond. The intermediate hydroperoxides are claimed to be soap stabilizers (Procter & Gamble U.S. Pat. 2,473,154).

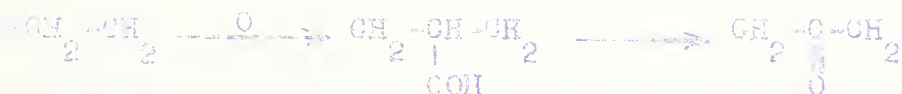
FISSION - B. SATURATED ACIDS, STEARIC AND PALMITIC

The fission products of the saturated acids have been relatively neglected. Generally, degradation products are uneconomical since the by-products formed are of little or no value, and the shorter chain products are available more cheaply from petroleum chemicals. A few notes and suggestions follow.

Saturated acids may be made to undergo oxidation with the formation of various degradation products. Generally speaking the ω carbon is first attacked giving rise to shorter chain acids. The activity of the ω carbon decreases with increased chain length so that by the time stearic acid is reached only vigorous oxidizing methods can attack the chain at all. This minimizes any slight directional forces that may be present and results in mixtures of degradation products which are not attractive economically. For example, the loss alone in weight through degrading stearic to palmitic acid, were it possible to so regulate the reaction, would represent a loss of 9% material and at 15% for stearic would make palmitic worth 16 $\frac{3}{4}$ %. For the same reason, myristic would be 18.7% and lauric 21.3%. This cost is for basic material alone without adding the cost of oxidation or fractional distillation. By the time lauric acid were reached in any oxidation procedure, large

quantities of lower acids would be turned to great losses from such sources would also have to be added to the costs. There is no point in speculating further on the costs of such procedure since research to date has not shown any practical way of accomplishing this purpose. Actually the cost ratio of coconut oil to tallow would have to be in the neighborhood of 2:1 before it would be feasible to even instigate serious research for this purpose. The same reasoning applies to nitric acid oxidation where the degradation products are chiefly the dibasic acids.

Some evidence exists that low temperature oxidation of the saturated acids can be made to yield hydroperoxides with the end product mainly ketones plus some alcohols



[See review by Swern et al J. Am. Oil Chemists' Soc. 25, 193 (1948)] but the importance as a commercial source of material is slender until the mechanism of the reaction has been more thoroughly studied so that the reaction can be controlled to give high yields of desirable products.

The most promising reaction is that of Dakin, [J. Biol. Chem. 4, 227-233 (1908) Am. Chem. J. 44, 41-48 (1910)] and later studied by Clutterbuck and Paper, [Biochem. J. 19, 385-396 (1925)] that indicated the ammonium salts of the higher acids could be made to yield α -ketone acids in the presence of hydrogen peroxide.



The reactivity of the ketone plus the fact that only one carbon is lost, suggests that the reaction be investigated further.

Fission products by pyrolysis of saturated acids are unimportant as a commercial source of new materials since the products obtained are equivalent to hydrocarbons and as such are obtainable more easily from petroleum sources. The bombardment of saturated acids with α particles [Sheppard and Burton J. Am. Chem. Soc. 68, 1636 (1946)] results in decarboxylation and has only theoretical interest. The writer also showed that α bombardment by use of radium did not cause any measurable elaidinization of oleic acid at room temperatures over severable months of contact. This information because of its negative nature, was never published.

Mention must be made of two additional fat products available recently in commercial supply - namely pelargonic acid and azelaic acids from the oxidation of oleic acid by chromic acid with subsequent reduction of the chromium sulphate by electrolysis. In my plant visit to Emery, this part was not shown. However, it was strongly hinted that a revolutionary process was at present under development. Speculation is that it may deal with a new type oxidation process possibly involving ozone or other oxidizing agent. This last gives the same fission products as chromic acid and has recently reached the headlines by a new method of manufacture. The amide of pelargonic acid would fall somewhat into the same general pattern as that of other fatty acids, except that it would be more easily reacted, of lower melting point and more water soluble. The diamide of azelaic acid however falls into the same category as adipic, and if it could be manufactured at a comparative price, would also have a potential use as a textile material. The raw material for adipic acid is benzene presently priced at about 7¢ per lb. If oleic at 17¢ (and very pure oleic must be used in the Emery process) yields 80% of fission products, then to clear a 5¢ per lb. manufacturing cost, exclusive of overhead, plant amortization, advertising and sales costs, would require a cost price of 24½¢ per lb. for azelaic when the manufacturing cost price of pelargonic acid is set at 20¢. This is arrived at in the following manner:

1 mole (282) of oleic acid yields 0.8 moles (126.4) of
pelargonic acid and
0.8 moles (150.4) of azelaic acid or

282 lbs. of oleic @ 17¢ costs	\$47.94	to this add
a 5¢ per lb. mfg. cost of	\$14.10	to yield a

Total mfg. cost of	\$62.04
--------------------	---------

126.4 lbs. of pelargonic acid @ 20¢ per lb. yields \$25.28
which leaves (\$62.04 - \$25.28) \$36.76 to be recovered from
150.4 lbs. of azelaic acid, corresponding to a mfg. cost
price of 24½¢ per lb.

On a 10¢ cost price for oleic acid (corresponding to a wholesale price of 6¢ per lb. on tallos) the same method of calculations would yield a price of 15¢ for pelargonic acid and 13¢ per lb. for azelaic acid.

With an allowance for sales, plant amortization, etc. overall, only this last condition (namely 6¢ tallos) would permit azelaic acid to approach competitively with that of petroleum derived adipic acid whose present sales price (after 1951) is approximately 25¢ per lb. Therefore unless azelaic acid has some unusual property over adipic acid as a plasticizing or textile material which would warrant a premium price, then prospects of a market in this field is limited unless fat prices fall considerably, which agrees with the present opinion here.

It should be pointed out that product development research must be balanced as far as possible to the percentage of products obtained. This policy was clearly pointed out by several examples encountered in the scale. For instance, in the Furfural Process used by Pittsburgh Plate Glass, the premium fraction of soybean drying oil obtained, had to carry the entire cost of the operation since the by-product (lower saturated glycerides) did not command the premium in the grade to which they were theoretically entitled. If a market were created for pelargonic acid for example, which warranted a price of 50¢ per lb. azelaic acid could be sold as a by-product to cover costs below 5¢. These figures must be considered only as directional. The yield of fusion products from oleic acid could not be obtained, but was placed at 80% through opinions outside Drery.

* Present sales prices (Drery Industries) drum lots fob Cincinnati are as follows:
Pelargonic acid-59 1/4 lb. Azelaic acid-61-3/4 lb.

4. SUBSTITUTION PRODUCTS

A. HALOGENATION

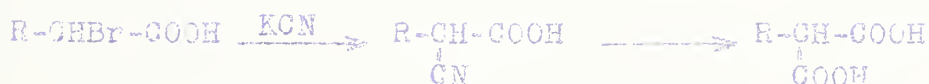
Chlorine, being the cheapest halogen, is the most important halogenation agent at present. Saturated acids generally are believed to substitute first on the α carbon. Once a halogen has entered, however, subsequent halogenation proceeds more rapidly with substitution taking place at random along the entire chain. The maximum substitution practical on a commercial scale is 5 (Hooker Electro Chemical). Above this, the chlorinated compound becomes unstable, and such products have a limited use. The carboxyl group is protected from chlorination by conversion to the methyl ester. Methyl penta chloro stearate is a plasticizer. It must be prepared from extremely pure stearic to avoid discoloration and for such purposes, the Hooker Electro Chemical Co. uses the Emery solvent crystallized, triple pressed grade.

Methyl dichlorostearate is also made by Hooker Electro-Chemical Co. for Continental Oil Co's. account, who hold patents on its use as an oil additive. Production of both type products above named consumes approximately 200,000 pounds of stearic acid per year, the pentachloro product being larger than the methyl dichloro one. It is believed that this represents the entire United States production.

The data on the salts and other esters of such chloro products were not available but it is felt that the use, while having good possibilities of increasing, will never consume very large quantities of stearic or palmitic acid.

Of more interest from this angle is the use of chlorine as an opening wedge in the solubilizing of stearic acid salts for soap use. Sodium stearate is a very poorly soluble soap which to some degree accounts for the large use of coconut oil in the soap industry. Work on this subject noted was that of Dr. Guest of the J. B. Williams Company who was interviewed. Data presented indicates that chlorine does not enter the α position of a stearic or palmitic ester with the same directional ease as does bromine, [Guest, J. Am. Chem. Soc. 66, 2074 (1944); ibid 66, 300 (1947)]. Patents assigned to Williams & Co. (U.S. Pat. 2,435,828-9) covers the reduction of α bromo stearic acid in benzene with

sodium in alcohol solution, such as propylene glycol, to yield water-solubilizing groups, which improve the water solubility, lathering power and detergency. The reaction of α -chlorostearic acid with alkanolamines is covered in U.S. Pat. 2,277,015. Since the halogen is lost in the reaction and since bromine is approximately five times the cost of chlorine (pound for pound) and ten times its cost on a molar basis, the latter material would be the only halogen practical in any present day large scale commercial use, irrespective of its non-directional qualities. Derivatives through bromine would be restricted to very special type products. Other common means are available for replacing the chlorine with a water-solubilizing group such as in α -hydroxystearic by means of alcoholic potash, α -dicarboxylic acid by adding KCN and hydrolysing it in the presence of a catalyst such as PCl_3 .



or by dehydrochlorinating according to the methods of Van Atta et al [J. Am. Oil. Chem. Soc. 24, 149-55, 209-12 (1947)] also Van Atta to USDA - U.S. Pat. 2,430,897 using a cobalt chloride-pumice catalyst at 220-280° and a reduced pressure of 1.0 to 1.3 mm. Dichlorostearic and dichloropalmitic acids gave 70.4 to 88.0% yields of unsaturated products containing from 0.7 to 8.4% residual chlorine, 2.6 - 6.7% unsaponifiable, less than 0.2% saturated acids and iodine values from 130.2 to 157.7. It was shown that the ester was harder to dehydrohalogenate than the acid, a factor not influenced by halide position, and that the soap produced had far greater foam power than coconut or oleic acid soaps and greater wetting power than soaps from oleic acid or Nacconol NRSF (a 90% active dodecyl benzene sodium sulfonate) and 14% greater detergency than coconut oil. This is a remarkable achievement since adding double bonds tends to lower detergency. This must be attributed to their position near the carboxyl group.

Three things are believed essential to make this a very satisfactory method of improving stearic and palmitic acid for soap use.

(1) Improvement in yields. Since the experiments were laboratory and pilot plant this problem would probably be one of plant design.

(2) Reduction of residual chlorine. This might be bothersome in a finished product and cause discoloration. Values in the range of 0.2% might be satisfactory.

(3) The double bond gives concern. The usual preparatory experience is that unsaturation tends to cause rancidity and off coloration. It would appear logical to block these by addition such as was done by Guest (U.S. Pat. 2,435,329) or better still by Swern et al (J. Am. Chem. Soc. 67, 1785-6 (1945)) who used H₂O₂ to convert oleins to 9,10-dihydroxystearic acid in 93% yield. 22 This method has been confirmed by Greenspan (Ind. & Eng. Chem. 39, 847-8 (1947)).

The solubility of stearic and palmitic acids would require only a gentle solubilizing agent to make them equivalent (in my opinion) to C₁₂-C₁₄ acids. Such substitution would be monochlorination and dihydroxy addition without recourse to the more drastic change typified in U.S. Pat. 2,445,892. There would be an accumulative effect which could conceivably reduce the overall chlorination dehydrochlorination and addition quite considerably.

An examination of costs on a two step, 20-ton per day plant capitalized at \$20 per ton year of production would be as follows.

1210*	lb. Hydrogenated tallow @ 8-3/4¢ / lb for	
	hydrogenation & splitting	\$118.00
293	" Chlorine @ 4.4¢	12.90
	Catalyst (est.)	.04
	Steam power & water	.59
	Labor @ \$2.00 per hr.	2.40
	Overhead 100% of direct labor	2.40
	Amortization of plant (10 years)	1.00
	Repair and Maintenance	.20
		<hr/>
		\$137.53

Present cost of tallow 8-3/4¢ July 23, 1951
of coconut oil 12 1/2¢

Estimated cost of derivative 13.75¢ per lb.

Efficiency of product 114% of coconut oil soap

Cost of derivative in terms of equivalent detergent
power of a coconut oil soap - $\frac{100}{114} \times 13.75 = 12¢$.

* Wt. of fat to yield 1150 lbs. of acids for 88% yield of product.

Hydrogenated tallow is used in the calculations shown. oleic present would preferably absorb the chlorine. In commercial operation the tallow would probably be continuously split, partially separated by solvent extraction or crystallization, the concentrated stearic run through the chlorinator, dehydrochlorinator and oxidizer and re-united with the red oil.

Even with this rough estimate, the process appears very promising. Reduction of the chlorine and use of 20¢ per lb. H_2O_2 should not alter the overall picture greatly.

An examination of this or similar type process [see also Ishii J. Soc. Chem. Ind. Japan 46, 859-91 (1943)] indicates possibilities in the following directions.

(1) To reduce the amount of coconut oil in soap. Present consumption is approximately 300 - 400 million lbs. per year. This would be a tremendous tonnage outlet possibility for tallow.

(2) To permit tallow substitution in present fat based alcohol sulfates. Estimated amount involved - 25 million lbs.

(3) In addition the process would re-open investigations on the use of stearic acid as a source of the fat radicle in Igepon T. Stearyl substituted amides would have to be re-evaluated etc.

Consideration is now given to the use of such α chloro substituted fatty acid for addition of an amine or other group. The introduction of a single hydroxy group would be of insufficient value as far as soap making properties are concerned to warrant the cost involved. On the basis of 4.4¢ per lb. chlorine, an estimated cost of producing a monoethanolamine derivative using such equipment as an (1) esterification kettle (2) chlorinator (3) dehalogenator and (4) saponifier with alcohol recovery would be quite considerable and could only be done on a large scale and with continuous equipment. Since the alcohol is recoverable and the additive forms a part of the product, cost of the process depends largely on the cost of the halogen versus utility of product. On the basis of a \$70 per ton year plant, the costs to convert 1000 lbs of stearic acid to the monoethanolamine derivative would be approximately as follows.

Using Chlorine Using Bromine

1000 lb. tallow @ 8-3/4¢ lb.	\$ 87.50	\$ 87.50
3.7 moles (540 lbs.) of Monoethanolamine @ 30¢	162.00	162.00
3.7 moles halogen @ 4.4¢ for Cl & 25¢ Br	5.76	74.00
Processing @ 1.5¢ per lb. acid used	15.00	15.00
Total	\$270.26	\$338.50

Yield approx. 1400 lbs.

Cost Per Pound

Raw materials	\$ 17.90	\$ 17.90
Halogen	41	5.35
Processing	1.07	1.07
	19.38¢	24.32¢

This indicates the necessity of using chlorine over bromine commercially and the importance of maintaining a low cost addition compound. Since solubilization is only one phase of the problem of utilizing stearic as a soap, the cost of production is still out of line with other comparative fat sources such as coconut oil and probably indicates why so little work has been done on such research. One point worth consideration in such a study however, and mentioned previously is the fact that a small percentage of a more soluble soap often has a tremendous general effect on the product. A small amount of myristic or lauric acid soaps for example have a great influence on the solubilization of stearic acid soaps. Even such an unusual salt as the p-octylphenoxyacetate will do this also (Procter & Gamble U.S. Pat. 2,263,729.) For this reason it is quite possible that only a partial conversion to a soluble stearate would be necessary.

Any large-scale application of the above would involve the use of a cheaper raw material than stearic acid. Since chlorine adds readily at the double bond before it would substitute, tallow would not be suitable unless it were hydrogenated at a cost of 1¢ - 1.5¢ or fractionally separated by solvent extraction, crystallization and/or interesterification methods. These last methods

are commercially available and could very well supply a raw material at a price within 2¢ of the market.

The discussion to this point has covered only substitution when the carboxyl group is blocked. When the acid itself is halogenated with Br in the presence of red phosphorous as a catalyst, substitution occurs both at the α position and at the carboxyl group. Palmitic acid gives α -bromo-palmitoyl bromide [Gantter & Hell, Ber. 24, 2209 (1891)]. Since oleyl chloride is a prime material for the manufacture of the detergent Igepon T and since stearoyl chloride is unattractive, due to the difficulty in condensing it and to its insoluble nature it is interesting to speculate on the possibility of utilizing an α substituted product for the reaction as discussed above.

Several factors dampening enthusiasm for this type of investigation is (1) the fact that chlorinations in general are expensive processes requiring special equipment and costly chemicals, hard to get under emergency conditions and (2) the parent detergent, Igepon T itself is not extensively used as a detergent because of the price relationship with other non-fat type materials. It is believed that success along these lines would depend either on a substantial drop in present tallow prices from 15¢, plus the stabilization of price, or in the production of a detergent material even superior to that of the oleyl methyl tauride (Igepon T).

TWO METHODS HAVE BEEN SUGGESTED FOR IMPROVING STEARIC ACID OR TALLOW FOR DETERGENT AND OTHER USES. ONE INVOLVES CHLORINATION, DEHYDROCHLORINATION AND OXIDATION. COSTS HAVE BEEN ESTIMATED ON A PROCEDURE USING THE FIRST TWO STEPS, AND IS NOT OUT OF LINE IN COSTS WITH PRESENT RAW MATERIAL PRICES. THE SECOND METHOD INVOLVES MONO-HALO SUBSTITUTION AND CHEMICAL REMOVAL WITH A GROUP WHICH IS NOT AN HYDROXYL. AN ESTIMATE SHOWS THE RELATIONSHIP IN COSTS BETWEEN CHLORINE, BROMINE, FAT AND ADDITIVE.

OF THE TWO METHODS, THE FIRST IS PREFERRED.

SECTION 3

EDIBLE ANIMAL FAT PRODUCTS

Table 8 below gives a brief summary of edible fat production and consumption for the period 1936 to 1949 as given by the Bureau of the Census. As pointed out by the Department of Commerce, large quantities of lard and tallow are produced locally and are not included in these figures. However, the data will be comparable to that given for inedible fats and will serve the purpose of obtaining a bird's eye view of the situation.

Table 8Factory Production & Consumption (In 1000's of lbs)*

Rendered Lard (including neut. lard and rendered pork fat)			Edible Tallow	
Year	Production	Inedible Consumption	Production	Inedible Consumption
1936	1,063,155	77	96,117	564
1937	896,474	207	78,114	857
1938	1,163,112	23	93,481	891
1939	1,413,751	80	95,825	1,264
1940	1,686,097	789	78,702	2,269
1941	1,622,989	91	91,139	6,766
1942	1,894,411	338	111,872	1,571
1943	2,163,410	88,347 (2)	130,804	5,298
1944	2,443,276	184,119 (2)	102,943	44,989 (3)
1945	1,315,523	82,416 (2)	114,735	33,412 (3)
1946	1,408,271	1,156	71,572	7,631
1947	1,781,308	7,472	94,985	8,070
1948	1,791,446	5,030	69,713	3,264
1949	2,184,000	(1)	105,562	(1)

* U.S. Bureau of the Census Data

(1) Not available

(2) Principally to soap use as follows: 1943-74038, 1944-176,266
and 1945-82070.

(3) Principally to soap use as follows: 1944-43761, 1945- 32,067.

This data shows the comparatively small production of edible tallow as against rendered lard - in all cases below 10% and in a few cases below 5%. The question of increasing the edible tallow production was considered. The opinion from the survey was that the present scale of production between edible and inedible tallow was in balance with the differential of about 1% in price between the two. Edible tallow has a greater stearin content than lard and finds its greatest use in shortening, being comparable to a slightly hydrogenated lard in this respect.

Without attempting at this point to discuss edible consumption, which figures will be given more clearly in Table 9 to follow, a total figure showing how much fat was diverted from edible to inedible use was included in Table 8. Except for the war years 1943-4-5 wherein large quantities of both materials were diverted to soap use (see footnote to Table) the total diversion is insignificant. We could leave this point therefore were it not for the fact that during 1950 considerable quantities up to an estimated 100 million lbs. (Fats & Oil Situation July 1951, P13) was used in soap. Swift and Co. estimated such usage during the last quarter of 1950 only, as 60 million lbs. This abnormal diversion is attributed to the soft price of lard during this period as compared to grease and to the fact that there has been a gradual shift from tallow to grease, during and subsequent to the war. This situation is explained in Section 1 Page 5 Paragraph 2.

Any shift however from hard to soft fats in soap or from inedible grease to lard, will not affect the overall animal fat situation in the least since animal fat merely replaces another animal fat and therefore needs no further comment here.

The edible uses to which fats and oils are put, may briefly be considered as in

- (1) shortening
- (2) margarine
- (3) mayonnaise
- (4) salad dressings
- (5) bakery goods
- (6) confectionery
- (7) commercial roasting and frying.

Table 9 illustrates this point.

Table 9*

Factory Consumption of Lard in
Edible Products. (In 1000's of lbs.)

Year	Total	In Shortening	In Oleomargarine	In other Edible Products
1936	7,318	4,503	2,198	471
1937	8,938	915	1,747	6,013
1938	9,925	2,825	1,461	5,518
1939	15,253	7,398	1,355	6,317
1940	29,519	16,786	5,098	6,587
1941	18,606	5,237	8,298	4,724
1942	51,221	30,094	8,134	7,999
1943	144,728	36,407	11,694	3,166
1944	243,738	38,729	9,631	3,166
1945	115,467	23,142	5,787	3,372
1946	29,172	20,387	2,058	4,781
1947	114,971	100,635	3,144	3,720
1948	125,870	113,996	3,498	3,346
1949	130,133	88,475	(1)	2,758

* U. S. Bureau of the Census reports
(1) Not available.

This table indicates that the factory consumption of lard shows an appreciable increase in shortening. Only during the war years did any significant amount of lard go into oleomargarine. The use of lard in other edible products is insignificant and the amount used has been steadily diminishing since 1937.

There is some consideration being given to the use of fat to supplement cat and dog food preparations. These must be considered as a non-edible fat outlet and are so classified by the Bureau of the Census (Animal & Vegetable Fats & Oils 1945-1949 P65). However, there has been no prior opportunity for discussion on this aspect of the problem. Efficient extraction methods have reduced the fat in many protein feed materials such as cracklings from a normal 7 to 8% by pressing or expeller means to about 2-3% by extraction means. This latter process is presently estimated to account for about 10% or 200 million lbs. per year of the total production of grease and tallow. (Source of estimate Mr. F. B. Wise, Sec. Treas. Nat. Renderers Assoc.). A few companies using this process include Swift & Co. Chicago, Darling & Co., Chicago, H. M. Rubin Co. New York, Detroit Rendering Co., Detroit, Minneapolis Hide & Tallow Co. Minneapolis and others.

Page 39

The reduction of fat content in extracted feed materials has reached a point that some additional fat or carbohydrate is required. Dr. Kraybill, of the American Meat Institute, said that this problem is under study, particularly the advantage of a fat over a carbohydrate addition to the feed, since carbohydrates in general cost about $\frac{1}{2}$ that of fats - on a calorific value. The market is surprisingly large. Data obtained principally from Dr. Kraybill follows: dog foods average about 5% fat content and are classified roughly as dry dog foods (4-5% fat content) and wet or canned dog foods (5-6% fat dry basis). Dry dog foods sell considerably more than wet dog foods. Bureau of Census data for 1947 give dry cat and dog food production at 680,712,000 lbs. valued at \$57,970,000 and wet cat and dog food at 427,137,000 lbs. valued at \$38,339,000. Present estimates place wet dog food production at 1,000,000,000 lbs. (H. R. Kraybill, Am. Meat Inst.) valued at \$75,000,000 (P. M. Lindeen and B. H. Carlson, A. C. Nielsen Co.) with the value of the dry product placed at \$125,000,000 (P. M. Lindeen et al). On the basis of the 1947 production of dry cat and dog food (680,712,000 lbs.) and a 4% fat content, then an increase to 15% fat content would indicate an additional use of 75 million lbs. of fat per year. Broiler poultry feeds contain about 3 $\frac{1}{2}$ % fat. An increase to 5 $\frac{1}{2}$ % would also represent a usage of 75 million pounds of fat on the present consumption basis. All poultry feeds, including broiler feeds contain about 3% fat. An increase of 1% fat content to 4% would represent an increased usage of fat up to 340 million pounds representing 34 billion pounds of feed a year.

The above avenue of investigation is interesting but not too promising since very positive physiological evidence would have to be forthcoming to establish a fat superior to carbohydrate under the conditions of use. In addition, it is necessary to consider only that portion of fat in excess of past usage, as supplying a new outlet. For example, if cracklings are reduced from 7 to 3% fat content and then the cracklings have to be fortified with 4% fat to bring them up to a feed standard, the 4% fat added cannot be considered a new outlet since the same equivalent of fat has been added to production.

Referring again to Table 9, it was noted that the usage of lard in shortening has been steadily climbing. This is due chiefly to the compounded lard products now being placed on the market by the large packers; SWIFT'NING for example by Swift & Co. Armour plan to bring out a similar product shortly, possibly Armix now being test marketed. Table 10 following shows the relation between butter, shortening, lard, margarine and miscellaneous edible oils such as salad oil, roasting fats etc.

Table 10*

Civilian Consumption (in millions of lbs.)

Year	Butter(2)		Lard as		Margarine		Shorten-		Edible		Total	
	Fat		such				ing		Oils			
	Basis	Per		Per		Per		Per		Per		Per
	wt.Capita		wt.Capita		wt.Capita		Wt.Capita		wt.Capita		wt.Capita	
1926	1701	13.2	1442	11.2	322	2.5	1580	12.3	732	5.7	5757	44.5
1927	1706	13.2	1358	10.8	326	2.5	1580	12.3	818	6.3	5758	44.7
1928	1729	13.3	1436	11.0	312	2.4	1490	11.5	900	6.8	5738	44.0
1929	1832	13.9	1662	12.6	213	1.8	1396	10.8	946	7.2	6077	46.2
1930	1806	13.6	1801	14.3	256	1.9	1185	8.9	997	7.5	6045	46.3
1931	1702	12.9	1819	13.7	294	2.2	1368	10.5	1100	8.3	5883	45.1
1932	1685	12.7	1689	12.8	296	2.2	1277	9.2	1001	7.6	5807	44.6
1933	1228	9.5	1678	13.0	408	3.1	1234	9.5	818	6.3	5396	41.6
1934	1233	9.6	1583	12.3	404	3.1	1117	8.9	871	6.6	5239	40.5
1935	1139	8.8	1510	11.6	426	3.3	1175	9.1	803	6.2	5053	38.9
1936	1175	8.5	1645	11.8	433	3.1	1409	10.1	870	6.2	5531	39.7
1937	1292	9.0	1816	12.7	580	4.0	1338	9.2	997	6.9	6023	42.0
1938	1171	8.1	1885	12.9	717	4.9	1411	9.6	1052	7.2	6236	42.6
1939	1253	8.5	1750	11.8	692	4.6	1435	9.6	1209	8.1	6339	42.7
1940	1316	8.7	1921	12.7	742	4.9	1655	11.0	1354	9.0	6989	46.3

* From Fats & Oils Situation #148 April 1951 P.19 as modified

(1) Preliminary

(2) Used 80.5 to convert actual wt. to fat basis from original table.

An examination of this Table shows (1) the relative stability of the per capita consumption of all fats, if we consider the war years abnormal ones (2) the steady decrease in butter consumption (3) the steady consumption of lard, hardly affected by the war period, (4) the steady increase in margarine relatively unaffected by the war years and in an amount just sufficient to balance the decrease in butter if we consider the ratio of substitution as 2 lbs. of butter for 1 lb. of margarine (See Fats & Oils Situation Department of Agriculture #140 February-March-April 1950 P 19); (5) the slight drop in shortening manufacture, accentuated by war conditions and (6) the rapid increase of fats for miscellaneous edible use such as in salad dressings, mayonnaise etc. The following tabulation in round figures, as I interpret Table 10, is given, which help illustrate points 1 to 6 above.

Trends Indicated from Table 10
in terms of per capita consumption in lbs.
for the period 1936 - 1950

	Butter	Lard	Margarine	Shortening	Oil Products	Total
1936	13	12	3	12	6	46
1940	9	12	5	11	9	46
Decrease by	4	-		1		-5
Increase by			2		3	+5

Considering the interpretation given by FOS #140 P 19 as correct, (see point 4 above) then the slight drop in shortening must be considered as more than compensated for by the decided increase in miscellaneous edible products which for the most part are made from vegetable oils. The situation in regard to lard itself is stable. Since consumption is stable, any great increased use of animal fats, particularly lard, would have to come through displacement of either butter fat or vegetable oils. The present trend is to use the cheaper and more available lard in shortenings. In pre-war years this amounted to 16 million pounds, by 1949 it had grown to 127 million pounds and in 1950 was 170 million pounds (Fats & Oil Situation #150, July 1951 P12). The use of lard in margarine and other edible products has not been promising to date either percentage wise or in total tonnage. The question now arises as to how far such conversion would go, before the use of lard itself as a cooking fat would be curtailed. This obviously raises points beyond the scope of this report. However, for the purposes of laying a foundation for the discussion to follow on the technical aspects of lard in shortening, a brief summary of possible trends is outlined here, as disclosed by interviews and the data gathered in the course of this study. In the first place, the processing of lard to a shortening increases its value. This is highly desired by the packer. As

more and more lard is siphoned from production for this purpose the price will strengthen until such a point is reached that its use in soap for example or for exports would be curtailed. The point where the use of lard itself as a cooking aid pulls away from its present 12 lbs. consumption per capita would have to be considered as the upper limit for an increased use of lard for any purpose whether edible or inedible. Under these circumstances we are considering that lard as an edible product is much to be preferred over lard as a soap base material or as an export item. On this basis, the present potential market for lard in shortening would be about 30% or approximately 800 million pounds per year as indicated in Table 11 below.

Table 11⁽¹⁾

Lard & Rendered Pork Fat Supply (in millions of lbs.)
& Disposition in Per Cent

Year	Total Disappearance	(2) Export	In % of Total Used as Lard	Used in ⁽³⁾ Ed. Products	Used in ⁽³⁾ Inedible Products
1936	1586	8.6	91.0	0.4	>0.1
1937	1524	10.7	99.1	0.2	>0.1
1938	1674	13.9	95.8	0.3	>0.1
1939	1978	15.6	94.0	0.4	>0.1
1940	2156	10.8	98.1	1.1	>0.1
1941	2323	18.3	79.2	2.5	>0.1
1942	2491	27.6	69.6	2.8	>0.1
1943	2679	29.7	65.1	1.9	3.3
1944	2895	32.4	59.3	1.8	6.5
1945	2393	28.1	67.2	1.3	3.4
1946	2157	22.7	76.2	1.1	0.1
1947	2369	17.7	77.6	4.5	0.2
1948	2349	13.9	80.9	5.0	0.2
1949	2595	25.7	68.4	4.7 ⁽⁴⁾	1.2
1950	2649	19.7	70.6	6.4 ⁽⁴⁾	3.3

(1) Based on data from FOS150 July 1951 Table 8.

(2) Total supply including imports adjusted for stocks.

(3) Split between edible and inedible proportionate to that given in Bureau of Census reports for same periods.

(4) Used figure of 127 million and 170 million pounds to shortening use in 1949 and 1950 respectively with balance to inedible (practically all to soap.)

It is the consensus of lard producers and independent investigators who have worked with both lard and vegetable oils in shortening manufacture, that lard may be processed to as good a shortening as a vegetable oil. Originally lard of course, was considered the ideal shortening, and when the process of hydrogenation was first introduced commercially in America, around 1910 or a little later, the object was to make a product from cottonseed oil or other edible oil then available, as close as possible to lard in color, texture and other characteristics. Originally the fact that the product was made from vegetable oil was kept secret to avoid prejudice against it by the consumer. The method used was to hydrogenate the refined and bleached oil to a low iodine value such as 15 or 20 and then to blend it with unhydrogenated or partially hydrogenated refined and bleached oil in such proportions that the final product would have a melting point about 30-35° C. It was later discovered that a product having superior keeping qualities was better made by slightly hydrogenating the entire oil to the same melting point. Generally the iodine value, which is a measure of the unsaturation, was lowered from about 105-115 to about 65-75. In the first case, the blended oils still contain about 80% or so, unhardened or partially hardened oil which contains a high percentage of unsaturates - particularly of linoleic and linolenic glycerides. In the second case, the hydrogenation has a chance by the selectivity of the process, to remove the highly unsaturated glycerides before large portions are converted into undesired stearates, isocoleates and elaidates. Within a few years, the technical development of vegetable based shortening had grown to a point where it was clearly superior to lard in keeping qualities, texture, uniformity and even in shortening properties by the use of emulsifiers (Procter & Gamble about 1933). Most of these advantages of a vegetable shortening were due to processing. Since the oil required hydrogenation, the process could be adjusted to a point where the melting points could be held within very close limits. As for example, within a few tenths of a degree centigrade. Refining and bleaching operations enabled close control of free fatty acids and colors. Deodorization, gave bland products. Lastly, crystallization operations where the oil was quick chilled, in such devices as the "Votator" permitted air to be incorporated within such close limits as 2%. The combined effect of several such factors (melting point, air content, chilling methods etc.) permitted very close control of the consistency of the product. The consistency and melting point could be varied for example to suit the season. Such processing made it possible to tailor products to different specifications to suit varying trade and retail requirements. The term "from purely vegetable oils" became synonymous with quality of product and commanded a premium price over lard. Lard lacks natural anti-oxidants and is less stable than the vegetable oils

for this reason, even when the amount of unsaturates is the same as in a vegetable oil shortening. Lard also varies in characteristics (iodine value, melting point and stability) within a fairly wide range depending largely on the methods of rendering, selection of the stock and on the diet of the hog from which the fat is obtained.

The principal advantage of lard is that it is a fairly good shortening without recourse to expensive processing and can therefore be marketed cheaply. This accounts largely for its present extensive use. For example, in a survey covering 1600 families in 68 cities (Home Nutrition and Home Economics of the USDA through Fats & Oils Facts, Am. Meat Institute Sept. 1949 issue, Chart 150) the weekly consumption of lard was from two to four times as high in families with a net income of \$1000, than with those families having a net income of \$5000.

LARD AS A SHORTENING AND MARGARINE MATERIAL

The consensus as to the merits of lard as a shortening material seems to be that if properly processed it is as good as a vegetable shortening. Proper processing means to

- (1) stabilize it against rancidity
- (2) hydrogenate it to proper consistency
- (3) deodorize it properly
- (4) package it attractively.

Point (1) is done by adding any one of numerous stabilizing agents as for example the American Meat Institute's TENOX 2, developed jointly with Tennessee Eastman. About 1 pound is used per ton of lard (Dr. Kraybill). Other stabilizing agents include such material as ground creosote bush which contains 7% dihydroguaiaretic acid (Cudahy, U.S. Pat. 2,457,741), tannic acid (Wilson, U.S. Pat. 2,354,719) deodorizer sludge (General Mills U.S. Pats. 2,363,672 and 2,377,029-30-31) gum guaiac (Ind. Pats. Corp. U.S. Pat. 2,377,610) citrus fruit (Swift U.S. Pat. 2,461,080) or dodecyl gallates (U.S. Pat. 2,483,099 to USDA).

The results to date of stabilization of lard have been very satisfactory and indicates that a solution to this most important problem exists. The edibility of the anti-oxidant used has not been questioned by the trade as far as this survey disclosed although investigations along this line is being carried out (S. C. Allen et al J. Am. Oil Chem. Soc. 28, 304).

Point (2), hydrogenation. Lard is not uniform from season to season or geographically. Hence lard had a bad time competing with a hydrogenated vegetable oil whose consistency could be duplicated to a few tenths of a degree centigrade. By hydrogenating a lard fully and then blending this with an untreated lard, the consistency can be made uniform and still retain some of the 10% or so linoleic acid present in the original lard, for nutrition value. (This method appears to be a convenience rather than a procedure designed for best results. It is cheaper for example to fully hydrogenate and blend since a smaller quantity of the lard is handled through the hydrogenation process. It is often more convenient also. For example, Swifts used this procedure with Swift'ning at the time of the interview. It was convenient to ship fully hydrogenated lard from a central plant to distant points for blending with the unhydrogenated lard. This saved transportation charges on moving a larger bulk of material and it saved capital expenditure for setting up hydrogenation units at distant plants. This is a very real problem, particularly to small packers. However, experience teaches that an all hydrogenated vegetable oil is superior in keeping qualities to a blended product when made from fully hydrogenated vegetable oil (iodine value 15 to 20) and an unhydrogenated oil or even with a partially hydrogenated vegetable oil. There is no reason to believe that lard would behave differently. In addition, it is questionable if the benefit of the few per cent linoleic acid remaining in the lard by design (according to the Meat Institute's recommendation) would not be offset by the increased stearic acid content of the highly hydrogenated fraction. It is well known that such products have low nutritional value. At the same time it is recognized however, that the problem of reducing the unsaturation of a lard such a small fraction as 5 to 10 points in iodine value, presents a major technical and economic problem. This is particularly enhanced by the fact that lard varies so widely in this characteristic (53 to 77 by Am. Oil Chemists Methods - Table 1-1-46). The solution to this problem probably lies in a more easily controlled and continuous hydrogenation procedure than that which is at present available. It is believed that research along such lines would be of great value).

No. (3) Deodorization. This is a problem with small manufacturers but not with larger ones. It is essential to produce a product comparable to a vegetable shortening.

No. (4) Packaging. This is being handled with skill by Swift & Co. Armour expect to follow suit.

The shortening value of lard is superior to vegetable products and it requires less creaming in the vatator (Slaughter-Girdler Corporation).

An emulsifying agent, such as the monoglycerides of lard should be incorporated to the extent of a few % to bring the creaming value up to that of vegetable shortening. It is not known how far the packers have gone in this direction. Swift's is 98% lard. It is quite possible that the other 2% is a monoglyceride plus stabilizer. Since the shortening power of lard is considered to be superior to vegetable shortening (Girdler Corp.) the requirement in this respect may be small. It is known (Procter & Gamble) that practically all shortenings today do contain emulsifiers which in general are the mono and diglycerides of the oils or fats used in the original products. Distillation products, for example, make a monoglyceride from cottonseed oil for use in vegetable oil shortening, one from fully hydrogenated lard for use in margarine and one from lard for use by bakers for pre-mixing.

In regard to packaging and marketing, several problems appear. The package should be designed to maintain maximum keeping qualities to relieve as much load on the anti-oxidant as possible. The vegetable shortening methods are worth studying. The use of the term "lard" when the product has been processed appears to offer a decided handicap by the packers. Several firms spoke with considerable heat over the restrictions imposed on them by the Meat Inspection Board - so much so in fact that it is believed here that a prime requirement to full use of edible tallow and lard in shortening would be a clarification of the regulations.

S U M M A R Y

SECTION 1

INEDIBLE FATS FROM ANIMAL SOURCES

Approximately 80% of all inedible tallow and grease is used in soap, 10% goes to fatty acid production and 10% to miscellaneous industrial uses. Although a definite trend toward the use of softer fats, such as grease and lard, in soap manufacturing has been noted, the total consumption compared with the total domestic disappearance has remained constant. Increased demands for detergents has been met by Syndets (Synthetic Detergents). It is estimated that if Syndets were not available, an added 350 million pounds of Inedible Tallow and Grease would have been required in 1949 to meet the demand. The present growth of Syndets is such that a further 30 million pounds of animal fats is being displaced yearly (3), practically all of which is in the soap powder field (6). Very probably a production of 2.0 billion pounds of Syndets, representing a displacement of 550 million pounds of animal fat (32) may ultimately be reached. Although the use of animal fats in Syndets is increasing, the estimated total use for this purpose will remain negligible in tonnage (8). Substitution reactions such as halogenation may prove great value in increasing animal

fat use in soaps (80-84) or synthetics (85).

Total fatty acid production in 1949 was approximately 600 million pounds (9). An examination of fatty acid uses (11-13) indicates a fertile field for investigation, particularly as any wide scale expansion would draw on the animal fats as a source of raw material (10). A more intensified research program on animal fats appears necessary (15-17). Various factors hinder such work, chief of which is the unstable price structure (13-14).

Research on processing methods indicates the solvent crystallization process as developed by the M. J. Kellogg Company is worth special consideration (20). Chemical bleaching (18-19) has raised controversial points which require further elucidation.

SECTION 2

FATTY ACIDS & DERIVATIVES

Production is largely confined to high pressure hydrolysis or the Twitchell method (23). This last must now be considered obsolete. Separation of animal fatty acids is largely done by solvent crystallization using acetone or alcohol. Pressing methods are obsolete (24). Other methods of interest include crystallization from a non-polar solvent (25) and by chromatographic means.

Of the carboxyl modified derivatives of the fatty acids the following deserve special attention from the point of view of production.

- (1) The monoglycerides and ethylene oxide derivatives as emulsifiers for food (30).
- (2) The metallic salts for use in lubricants (38).
- (3) Substituted amides as detergents (49).
- (4) Amine salts as non-metallic ore flotation agents (68).
- (5) Pyrolysis of heavy metal salts to alcohols (37).

Research should be directed so as to produce products not competitive with short chain products (48 & 70) or where the substantive or cationic property of the amines is an advantage (71).

Five types of research are mentioned (32-33) which will have a tendency to improve soap and strengthen its overall position, and a few non-fat petroleum derivatives are mentioned, the most important of which is the Du Pont synthesis of fatty acids from ethylene and a short chain acid such as acetic (62). The most important additive to fatty acids or its derivatives is ethylene oxide (65).

Summaries appear as follows:-

Esters (30)

Salts (34 & 38)

Amides (48-50)

Nitrile (59)

Amines (64, 70-71)

Alcohols (75)

Internal chain modification is studied in respect to saturated and unsaturated acids. Elaidinization is not considered promising (76), addition reactions involving hydrogen are the best known. With other materials the derived products are highly specialized in use (77). Fission products of oleic yield azelaic and pelargonic acids (77-79) whose derivatives are very important. Oxidation products of the saturated acids are important and require further study (79) as does also the substitution reactions involving the halogens (80-85). The position of this last is summarized on page 85.

SECTION 3

EDIBLE ANIMAL FAT PRODUCTS

Edible tallow and lard production with small exception (87) is fixed by factors beyond that of supply and demand. Only a minor fraction is used in normal years for inedible purposes (86). The total consumption of fats is limited (90) so that any great increased use of one fat would be made at the expense of another. Both lard and shortening have reached a dominant and stable position (90). The most interesting post war use of edible fats is the use of lard as a base material in shortening (92 Table II). Latest available data shows this use to be 6.4% of total disappearance. It is estimated that it could reach 30% (92).

The technical development most responsible for this new use may be attributed to the use of stabilizers (93-94). Other processing factors include deodorization, hydrogenation, packaging and marketing. These have been solved to a point where a satisfactory product is being made (94). Further work suggested, is the development of an hydrogenation process particularly suitable for lard (95) and the greater clarification of the terminology involving lard derived products (96).

The use of fat as an ingredient of animal feeds is briefly discussed (88-89).

Patents Referred to in the Report

<u>Patent No.</u>	<u>Page Reference</u>	
1,762,742	61	W.Reppe (to I.G.Farbenindustrie)
1,813,454	23	V.R.Kokatnur
1,883,820	36	A.A.Epstein (to Consolidated Patentees Inc.)
1,991,955	56	A.W.Ralston (to Armour & Co.)
2,005,619	73	G.D.Graves (to Du Pont)
2,019,022	72	N.D.Scott et al (to Du Pont)
2,033,536	56	A.W.Ralston et al (to Armour & Co.)
2,033,537	56	" " " " " " " " " " " "
2,043,965	62	K.Smeykal (to I.G.Farbenindustrie)
2,053,045	52	A.W.Ralston et al (to Armour & Co.)
2,053,046	52	A.W.Ralston et al (to Armour & Co.)
2,054,638	45	E.Schirm (Deutsche Hydrierwerke A.G.)
2,061,314	52	A.W.Ralston (to Armour & Co.)
2,078,922	61	H.R.Arnold (to Du Pont)
2,086,690	67	J.Zerwick et al (to General Aniline)
2,088,325	68	J.E.Kirby (to Du Pont)
2,101,314	67	A.Grun (to Am. Hyalcol Corp.)
2,104,421	63	A.Grun (Bohme Fettchemie)
2,120,512	44	E.Rosenhauer (to Henkel & Cie)
2,122,644	60	J.Harwood (to Armour & Co.)
2,132,388	45	G.J.Berchet (to Du Pont)
2,132,849	52	C.H.Greenwalt (to Du Pont)
2,132,902	58	S.Lenher (to Du Pont)
2,135,327	52	V.Conquest (to Armour)
2,143,751	61, 52	H.Adkins (to Rohm & Haas)
2,145,802	56	A.W.Ralston (to Armour & Co.)
2,145,803	56	" " " " " " " " " " " "
2,145,804	56	" " " " " " " " " " " "
2,159,967	67	M.Engelmann (to Du Pont)
2,162,971	58	A.W.Ralston (to Armour & Co.)
2,166,093	52	J.Harwood et al (to Armour & Co.)
2,175,092	58	A.W.Ralston et al (to Armour & Co.)
2,175,093	53	" " " " " " " " " " " "
2,177,407	26	V.L.Hansley (to Du Pont)
2,177,619	51, 52	O.Nicodemus et al (I.S.Farbenindustrie)
*2,039,212	42	J.Kritchevsky (to Minol Corp.)

<u>Patent No.</u>	<u>Page Reference</u>	
2,178,139	42	A.K.Epstein (to Emulsol Corp.)
2,178,522	54,58	A.W.Ralston et al (to Armour & Co.)
2,180,730	28	H.L.Cox (to Union Carbide & Carbon)
2,187,244	73	V.Mills (to Procter & Gamble)
2,190,921	74	B.R.Harris (to Emulsol Corp.)
2,191,295	69	H.Dohse (to I.G.Farbenindustrie)
2,192,664	42	J.Kritchevsky (to Ninol Inc.)
2,195,573	29	" " " " " "
2,198,806	46	A.K.Epstein et al (to Emulsol Corp.)
2,200,298	74	E.A.Robinson (to Nat. Oil Prod. Co.)
2,200,390	18	S.E.Freeman (to Pittsburgh Plate Glass)
2,200,391	18	" " " " " " " "
2,202,826	38	O.L.Brandes (to Gulf Res. & Dev.)
2,203,641	74	R.Kapp (to Nat. Oil Prod. Co.)
2,203,642	74	" " " " " " " "
2,205,076	52	C.G.Wortz (to Du Pont)
2,206,351	51	R.Greenhalgh (to Imperial Chem.)
2,208,598	54	G.W.Rigby (to Du Pont)
2,209,383	69	L.H.Bock (to Rohm & Haas)
2,212,654	45	W.V.Wirth (to Du Pont)
2,214,254	73	V.Mills et al (to Procter & Gamble)
2,219,879	61	B.M.Vanderbilt (to Commercial Solvents)
2,221,377	74	B.R.Harris (to Emulsol)
2,221,485	68	J.E.Kirby et al (to Du Pont)
2,222,728	68	F.X.Tartaron (to Phos. Rec. Corp.)
2,224,925	23	R.H.Fotts et al (to Armour & Co.)
2,224,984	23	" " " " " " " "
2,224,986	23	" " " " " " " "
2,227,823	28	H.L.Cox (to Union Carbide & Carbon)
2,229,307	66	A.W.Ralston et al (to Armour & Co.)
2,231,979	73	E.Wolter (to Procter & Gamble)
2,235,098	73	R.L.Brandt (to Colgate-Palmolive-Peet)
2,235,534	73	K.L.Russell et al (to " " ")
2,237,729	28	T.W.Evans et al (to Shell Dev. Co.)
2,247,711	69	A.W.Ralston (to Armour & Co.)
*2,232,485	42	J.H.Shipp (to Du Pont)

<u>Patent No.</u>	<u>Page Reference</u>	
2,263,729	33,84	W.Hentrich (to Procter & Gamble)
2,266,136	45	M.Weisberg (to Alrose Chem. Co.)
2,266,591	29	B.W.Eckey et al (to Procter & Gamble)
2,267,965	44,46,42	A.L.Wilson (to Carbide & Carbon)
2,271,619	23,26	G.B.Bradshaw et al (to Du Pont)
2,274,058	68	M.T.Goebel et al (to Du Pont)
2,277,015	81	H.H.Guest (to J.B.Williams Co.)
2,278,309	18	S.E.Freeman (to Pittsburgh Plate Glass Co.)
2,278,372	61	J.F.Olin (to Sharples Chem. Co.)
2,278,373	61	J.F.Olin (to Sharples Chem. Co.)
2,279,314	46	L.F.Henderson et al (to Lever Bros.)
2,280,850	52	A.W.Ralston et al (to Armour & Co.)
2,287,219	60	H.P.Young et al (to Armour & Co.)
2,289,044	74	J.Ross (to Colgate-Palmolive-Peet)
2,291,461	18	S.E.Freeman (to Pittsburgh Plate Glass Co.)
2,293,676	24	L.D.Myers et al (to Emery Ind.)
2,297,864	44	H.Beck (to Heberlein Pat. Corp.)
2,293,281	68	H.M.Corley et al (to Armour & Co.)
2,298,501	24	L.D.Myers et al (to Emery Ind.)
2,302,697	46	M.Katzman (to Emulsol Corp.)
2,304,304	29	J.H.Fritz (to Nat. Oil Prod.)
2,304,369	46	W.L.Morgan (to Arnold, Hoffman & Co.)
2,304,830	68	M.Katzman (to Emulsol Corp.)
2,305,830	61	E.Profft (to Alien Prop. Custodian)
2,307,047	46	M.Katzman et al (to Emulsol Corp.)
2,308,116	37	I.Silverman (to L. Sonneborn Sons Inc.)
2,313,360	68	A.W.Ralston et al (to Armour & Co.)
2,313,636	18	S.E.Freeman (to Pittsburgh Plate Glass Co.)
2,315,734	69	A.W.Ralston et al (to Armour & Co.)
2,316,512	18	S.E.Freeman (to Pittsburgh Plate Glass Co.)
2,317,301	69	A.W.Ralston et al (to Armour & Co.)
2,317,666	37	A.W.Burwell et al (to Alex Corp.)
2,320,009	69	A.W.Ralston et al (to Armour & Co.)
2,320,010	69	" " " " " " " "

Patent No.	Page Reference.	
2,321,020	76	E.E.Greger et al (to Colgate-Palmolive-Peet)
2,322,056	23	R.H.Potus (to Armour & Co.)
2,325,489	29	J.T.Eaton (to E.F.Houghton & Co.)
2,328,021	68	M.Katzman (to Emulsol Corp.)
2,329,086	45	E.A.Robinson et al (to Nat. Oil Products)
2,329,406	45	E.A.Mauersberger (to Alframine Corp.)
2,340,343	37,73	A.S.Richardson et al (to Procter & Gamble)
2,340,344	35,37,73	" " " " " " " " " " " "
2,352,160	24	A.C.Brown (to Emery Ind.)
2,354,719	94	B.I.Verbeck (to Wilson & Co.)
2,355,314	67	M.R.McCorkle (to Armour & Co.)
2,355,356	60	H.F.Yung (to Armour & Co.)
2,356,884	58	A.W.Kalston et al (to Armour & Co.)
2,356,903	29	R.C.Wood (to Procter & Gamble)
2,358,776	29	H.Goldstein (to L. Sonneborn Sons, Inc.)
2,363,047	44	M.DeGroote (to Petrolite Corp.)
2,363,672		I.L.Jakobsen (to General Mills Inc.)
2,365,290	78	D.Price et al (to Nat. Oil Products)
2,365,431	46	L.Orthner et al (to Alien Property Custodia
2,365,915	35	J.E.Taylor (to Procter & Gamble)
2,366,534	63	J.E.Kirby (to Du Pont)
2,367,366	61	J.F.Olin et al (to Sharples Chem. Inc.)
2,372,160	30	R.C.Morris et al (to Shell Dev. Co.)
2,374,213	29,46	M.Katzman (to Emulsol Corp.)
2,377,029		F.A.Norris (to General Mills Inc.)
2,377,030	94	F.A.Norris (to General Mills Inc.)
2,377,031	94	" " " " " " " " " " " "
2,377,610	94	L.C.Brown (to Industrial Patents Corp.)
2,381,314	30	W.H.Shields (to Emery Ind.)
2,383,525	53	N.B.Tucker (to Procter & Gamble)
2,383,526	53	N.B.Tucker (to Procter & Gamble)
2,383,579	23	H.D.Allen et al (to Colgate-Palmolive-Peet)
2,383,580	23	C.J.Arrowsmith et al (" " " " " " " " " " " ")
2,383,581	23	" " " " " " " " " " " "
2,383,596	23	E.E.Dreger (to Colgate-Palmolive-Peet Co.)

Patent No.	Page Reference	
2,383,599	23	G.A.Glossop (to Colgate-Palmolive-Peet Co.)
2,383,601	23	G.I.Keim (to Colgate-Palmolive-Peet Co.)
2,383,602	23	G.I.Keim et al (to " " " ")
2,383,614	23	J.H.Percy (to Colgate-Palmolive-Peet Co.)
2,383,632	23	W.R.Trent (" " " ")
2,383,633	23	W.R.Trent (to Colgate-Palmolive-Peet Co.)
2,383,737	53	A.S.Richardson (to Procter & Gamble)
2,384,443	30	J.C.Cowan et al (to USDA)
2,384,595	74	C.M.Blair (to Petrolite Corp.)
2,385,849	29	F.D.Snell et al (To Chemsearch Corp.)
2,387,537	69	H.G.Smith et al (to Gulf Oil Co.)
2,388,154	46	M.Katzman (to Emulsol Corp.)
2,388,400	74	F.C.Frank (to Socony-Vacuum Oil Co. Inc.)
2,389,191	78	J.D.Fitzpatrick et al (to Emery Ind.)
2,390,528	18	S.E.Freeman (to Pittsburgh Plate Glass Co.)
2,393,202	42, 44	L.A.Stegemeyer (to Emery Ind.)
2,398,254	29	N.K.Rosenthal (to Ninol Dev. Co.)
2,400,001	46	L.D.Grupelli (to National Oil Products)
2,401,756	23	J.K.Gunther (to Ind. Pats. Corp.)
2,402,526	69	J.Pike (to Du Pont)
2,403,293	46	J.J.Miskel (to National Oil Prod.)
2,408,959	54	L.A.Stegemeyer (to Emery Ind.)
2,410,096	76	R.E.Meyer et al (to Socony-Vacuum Oil Co.)
2,410,788	46	A.L.Morgon et al (to Arnold, Hoffman & Co.)
2,410,789	46	" " " " " " " " " "
2,414,393	51	R.H.Fotts (to Armour & Co.)
2,416,552	46	E.I.Valco (to Richards Chemical Works)
2,421,157	24	L.D.Meyers et al (to Emery Ind.)
2,423,232	18	S.E.Freeman et al (to Pittsburgh Plate Glass Co.)
2,427,821	30	J.B.Tindall (to Commercial Solvents Corp.)
2,430,675	18	G.A.Hempel (to Mathieson Alkali Works)
2,430,897	81	G.R.VanAtta (to USDA)
2,431,760	37	F.J.Licata (to Nopco Chem. Co.)
2,431,842	18	E.Stossel et al (to Mathieson Alkali Works)
2,433,243	69	H.G.Smith et al (to Gulf Oil Corp.)

<u>Patent No.</u>	<u>Page Reference</u>	
2,435,828	33,80	H.H.Guest (to J. B. Williams Co.)
2,435,829	33,80,82	" " " " " " " "
2,437,705	22	W.J.Paterson (to Lever Bros.)
2,437,706	22	" " " " " " "
2,443,063	25	D.E.Adelson (to Shell Dev. Co.)
2,443,184	24	E.W.Colt (to Armour & Co.)
2,444,828	52	W.Kaplan (to Sun Chem. Corp.)
2,445,892	82	D.Swern et al (to USDA)
2,448,602	37	E.B.Kester (to USDA)
2,450,235	24	W.P.Gee (to Texaco Devel. Co.)
2,450,611	23	R.H.Potts (to Armour & Co.)
2,450,612	23	" " " " " " "
2,450,858	78	J.D.Fitzpatrick et al (to Emery Ind.)
2,454,638	18	J.T.Dickinson et al (to M.W.Kellogg Co.)
2,455,374	17	L.H.Libby et al (to Lever Bros.)
2,457,741	94	J.R.Shipner (to Cudahy Packing Co.)
2,458,484	77	D.E.Terry et al (to General Mills, Inc.)
2,459,054	25	C.C.Towne (to Texas Co.)
2,459,818	32,39	L.F.Henderson (to Lever Bros.)
2,460,772	51	L.A.Stegemeyer (to Emery Ind.)
2,461,080	94	M.M.Piskur et al (to Swift & Co.)
2,461,349	52	A.W.Ralston et al (to Armour & Co.)
2,461,495	46	D.E.Floyd (to General Mills Inc.)
2,462,758	29	J.D.Malkemus (to Colgate-Palmolive-Peet)
2,464,094	43	E.M.Meade (to Lankro Chem. Ltd.)
2,467,906	18	H.J.Passino et al (to M.W.Kellogg Co.)
2,468,012	68	A.F.Isbell (to General Mills)
2,468,436	58	J.D.Fitzpatrick et al (to Emery Ind.)
2,468,799	21	N.W.Ziels et al (to Lever Bros.)
2,473,154	78	W.Lange et al (to Procter & Gamble)
2,474,010	59	L.D.Myers et al (to Emery Ind.)
2,483,099	94	S.G.Morris et al (USDA)
2,483,253	39	H.H.Young et al (to Swift & Co.)
2,489,713	23	W.M.Leaders (to Swift & Co.)
2,499,984	77	E.M.Beavers et al (to Rohm & Haas Co.)

<u>Patent No.</u>	<u>Page</u> <u>Reference</u>
-------------------	---------------------------------

2,505,012	24	H.T.Spannuth (to Wilson & Co.)
-----------	----	--------------------------------

Brit. Pats.

425,927	61,62	W.W.Triggs (Rohm & Haas)
467,166	69	I.G.Farbenindustrie
499,130	45	" " " "
506,049	44	" " " "
512,022	67	" " " "
536,602	27	Hoffman La Roche
560,448	69	Warwick Chemical Co.
567,128	46	E.H.G.Sargent
577,879	19	Lever Bros.
577,880	19	Lever Bros.
578,102	22	" " " "
581,799	39	" " " "
582,699	35,37,73	Du Pont
584,939	73	Procter & Gamble
585,219	73	Procter & Gamble
585,219	73	" " "
586,799	37,73	Du Pont
605,848	62	" "

German Pats.

595,173	46	H.T.Bohme
648,088	61	I.G.Farbenindustrie

<u>Patent No.</u>	<u>Page</u> <u>Reference</u>	
-------------------	---------------------------------	--

French Pats.

782,302	69	Deutsche Hydrierwerke A.G.
783,008	69	I.G. Farbenindustrie

Swiss Pats.

210,976	45	Soc. pour l'ind. chim. a Bale
---------	----	-------------------------------

Dutch Pats.

51,865	21	Industrieele Exploitiemij
--------	----	---------------------------

NAME OF COMPANY (PROJECT 86)	Date	By*	Man Interviewed
1. Advance Solvent & Chem. Cor. 245 Fifth Avenue New York, N. Y.	2/14/51	McC	A. B. Nullaly, Pres.
2. Alox Corp. Buffalo Ave. & Iroquois St. Niagara Falls, N. Y. (70 Pine St. New York 5, N.Y.)	3/2/51	McC	Leigh K. Lydecker, Pres. (Letter)**
3. Alrose Chemical Co. P. O. Box 1294 Providence, R. I.	3/23/51	McC	H. W. Lussman, Dir. of Research
4. American Cyanamid Co. 30 Rockefeller Plaza New York 20, N. Y.	2/28/51	McC	C. I. Davis, Pres.
5. American Meat Institute The University of Chicago 939 East 57th St. Chicago 37, Ill.	12/14/50	McC	Dr. H. R. Kraybill, Dir.
6. Archer-Daniels-Midland Co. Roanoke (600) Bldg. Minneapolis 2, Minn.	12/7/50	McC	Dr. S. C. Sorensen, Vice- Pres. O. H. Brownlee
7. Armour & Co. Union Stockyards Chicago, Ill.	12/15/50	McC	W. W. Spret, Pres. Dr. M. E. McCorkle, Dir. Res. J. D. Forsche, " " E. W. Wilson, Vice-Pres. C. W. Hoerr, " " L. C. Minney, Ass't Chair.
8. Armour Research Foundation of Illinois Instit. of Tech. Technology Center Chicago 16, Ill.	12/14/50	McC	
9. Arnold, Hoffman & Co. Inc. 55 Canal St. Providence, R. I.	3/23/51	McC	G. A. Rawcliffe, Ass't. Treas.
10. Atlantic Refining Co. 260 S. Broadstreet Philadelphia, Pa.	3/7/51	McC	J. F. McGrogan
11. Atlas Powder Co. Wilmington 99, Del.	11/15/50	McC	Dr. R. S. Rose, Jr. Dir. of Res. Dr. Barker

475 FIFTH AVENUE NEW YORK 17, N. Y.

	NAME OF COMPANY (PROJECT 86)	Date	By	Man Interviewed
				Dir.
12.	Battelle Memorial Inst. Columbus 1, Ohio	3/15/51	McC	Dr. Frank C. Croxton, Ass't Dr. Garson Lutz Dr. B. W. Consee, etc.
13.	Beacon Co. 97 Bickford St. Boston 30, Mass.	3/22/51	McC	A. Blake, Chemist
14.	Blaw Knox 321 Penn Ave. Blaw Knox Bldg. Pittsburgh, Pa.	12/28/50	McC	Keater McCubbijn, Mgr. of Fats & Oils Div.
15.	Carbide & Carbon Chem. 30 E. 42nd St. New York 17, N. Y.	2/16/51	McC	C. P. McClelland, Sales Devel
16.	Celanese Corp. of America 180 Madison Avenue New York 16, N. Y.	3/29/51 No	McC	C. R. Dolmetsch, Ass't. to Vice-Pres. (Letter)*
17.	Ciba Company 627 Greenwich St. New York 14, N.Y.	2/27/51	McC	J. P. Ballor, Vice-Pres. G. Wiseman
18.	Cole Laboratories 42-259 Long Island City	No		
19.	Culgate-Palmolive-Peet 105 Hudson St. Jersey City 2, N. J.	3/26/51	McC	Mr. Little, Pres. Dr. E. E. Dreger J. H. Blakney T. A. Hoppe
20.	Consolidated Rendering 178 Atlantic Ave. Boston, Mass.	3/22/51	McC	H. A. Naugle, Pres. Mr. Johnson, Plant Supt. " " Chief, Chem.
21.	Corn Products Refining Co. 17 Battery Place New York 4, N. Y.	11/30/50 No	McC	H. Hellman (Letter)*
22.	Cudahy Packing Co. Union Stock Yards Omaha 7, Nebraska	No		
23.	Darling Company 4201 Ashland Ave. Chicago, Ill.	12/18/50	McC	Dr. L. Weatherhead, Dir. V. A. Revert Mr. Werle, Dir. of Res.

NAME OF COMPANY (PROJECT 86)	Date	By	Man Interviewed
24. Davies Young Soap Co. 400 No. Findlay St. Dayton, Ohio	3/16/51	McC	D.H. Young, Pres.
25. Distillation Products 755 Ridge Rd. West Roch. Rochester 13, N. Y.	3/20/51	McC	J.L. Edwards, Sales Mgr. Mr. Mees Ass't.
26. Don Baxter, Inc. 1015 Grandview Ave. Glendale 1, Calif.	9/29/50	McC	Arthur Cherkin, Vice- Pres. Dir. of Res.
27. Drackette Co. Cincinnati, Ohio	3/16/51	McC	Cooperative
28. Drew, E.F. & Co. Boonton, N. J.	3/5/51	McC	Dr. J. Barsky, Consultant
29. Du Pont de Nemours Wilmington 98, Del.	11/17/50	McC	E.H. Rigby, Devel. Dept.
30. Eldorado Oil Works 311 California St. San Francisco, Calif.	9/27/50	McC	J.L. Suppler, coordinato Chem. Div.
31. Emery Industries Inc. 4300 Carew Tower Cincinnati 2, Ohio	3/15/51	McC	J. Stoubert, Vice-Pres. Mr. Boyd, Sales Mgr. J.P. VanTuyke, Chem. Di
32. Emulsol Corp. 59 E. Madison St. Chicago 3, Ill.	12/1/50	McC	Benjamin S. Harris, Vice- Pres.
33. Fairfield Laboratory 417 Cleveland Ave. Plainfield, N. J.	3/22/51	McC	J. Woods, Pres.
34. Fels & Co. 73rd. & Woodlawn Ave. Philadelphia 42, Pa.	11/9/50	McC	J. H. Fels, Ass't. to Pres
35. Fine Organics Inc. 211 E. 19th St. New York 3, N.Y.	2/21/51	McC	J. H. Weiner, Pres.
36. Foster Wheeler Corp 165 Broadway New York 6, N.Y.	2/21/51	McC	J. H. Chapin, Gen. Sales De

NAME OF COMPANY (PROJECT 86)	Date	By	Man Interviewed
37. General Aniline & Film Corp. 247 Park Ave. New York 17, N.Y.			(Under General Dyestuff Corp.)
38. General Dyestuff Corp. 435 Hudson St. New York 14, N.Y.	3/5/51	McC	J. Healy, Market Research
39. General Mills 400 - 2nd Ave. Minneapolis, Minn.	12/7/50	McC	Whitney Eastman, Vice-Pres. Dr. D.H. Wheeler, Dir. Tech. Sa
40. General Tire & Rubber Co. Akron, Ohio	No		
41. GERAL Chem. Co. Chicago, Ill.	No		
42. Girdler Corp. 222 E. Broadway Louisville 1, Ky.	3/12/51	McC	J.D. Slaughter, Vice-Pres. Bruce Miller, Res. Dir. Don. McMichael, Chief Vot. Di
43. Glidden Co. 5165 .. Moffat St. Chicago 39, Ill.	12/16/50	McC	G.W. Davidson, Gen. Sales Mgr
44. Glyco Prod. Co. 26 Court St. Brooklyn 2, N.Y.	2/21/51	McC	H. Bennett, Pres.
45. Goodrich, B.F. Co. 578 S. Main St. Akron, Ohio	12/1/50	McC	C.B. McKeown, Mgr. Dept. G.L. Mason, Ass't.
46. Gross, A. & Co. 295 Madison Ave. New York, N.Y.	2/15/51	McC	Walter Hagedorn, Pres.
47. Hardesty, W.C. 41 E. 42nd St. New York 17, N.Y.	2/16/51	McC	Dr. Blumen
48. Hercules Powder Co. 929 King St. Wilmington, Del.	2/16/51	McC	Dr. George Rieger

	NAME OF COMPANY (PROJECT 86)	Date	By	Man Interviewed
49	Heyden Chemical Corp. 393 Seventh Ave. New York 1, N. Y.	3/22/51	L.S.	E.T. Peters, Mgr. Mark. Dev
50	Hollingshead Co. Camden, N.J.	No/		
51	Houghton, E.F. & Co. 303 W. Lehigh Ave. Philadelphia 33, Pa.	11/8/50	McC	Dr. J.T. Eaton, Dir. of Res. Mr. Bills
52	Huntington Laboratories Huntington, Ind.	12/5/50	McC	T.P. Annan, Sec. Treas.
53	Inst. of Shortening Washington, D.C.	No/		
54	Jacques Wolf & Co. P. O. Box 839 Passaic, N.J.	3/6/51	McC	Mr. Desmond, Vice-Pres. L.S.
55	Jefferson Chemical Co. 711 Fifth Avenue New York 17, N.Y.	2/12/51	McC	Dr. H.B. Sommer, Sales Dev.
56	Jergens, Andrew Spring Grove Ave-2535 Cincinnati, Ohio	3/16/51	McC	J.D. Nelson, Vice-Pres.
57	Johnson, S. C. Carnue St. Racine, Wis.	12/8/50	McC	Dr. R.W. Duruis, Res. & Dev. Mgr.
58	Kellogg, M. Jersey City 3, N.J.	2/26/51	McC	J. Dickinson
59	Kellogg, Spencer & Sons 100 Delaware Ave. Buffalo 5, N.Y.	3/20/51	McC	R.L. Terrill, Res. Dir.
60	Kessler Chemical Co. Inc. State Rd. & Cottman Ave. Philadelphia 35, Pa.	11/9/50	McC	L.W. Masum
61	Kohnstamm & Co. 91 Park Place New York, N.Y.	2/19/51	McC	Robert A. Phair, Vice-Pres.

NAME OF COMPANY (PROJECT 86)		Date	By	Man Interviewed
62.	Lever Bros. 80 Varick St. New York, N.Y.	12/28/51	McC	Mr. W.H. Burkhard, Vice Pres.
63.	Maywood Chemical Works 100 W. Hunter Ave. Maywood, N.J.	3/5/51 No/	McC	A.J. Turner, Sec. Treas.
64.	Mellon Institute 1400 Fifth Ave. Pittsburgh 13, Pa.	11/28/50	McC	Dr. G.W. Seagren " W.H. McKnight (All fellows A.B. Sterle Gerhardt
65.	Metasap Chemical Co. Logan & Davis Sts. Harrison, N. J.	See Nopco		
66.	Monsanto Chemical Co. St. Louis, Mo.	12/21/50	McC	Dr. F.F. Ogen, Dir. of Res. Dr. H.G. Johnson
67.	National Aniline 40 Rector St. New York 6, N.Y.	3/6/51	McC L.S.	L.H. Flett, Dir. of Dev.
68.	Ninol Labs. 1719 S. Clinton Sts. Chicago 16, Ill.	12/18/50	McC	Dr. H.L. Sanders, Tech. Dir.
69.	Nopco Chemical Co., Inc. Harrison, N.J.	3/9/51	L.S.	Dr. E.A. Robinson, Dir. of Res.
70.	Nutrition Research Lab. Chicago, Ill.	No/		
71.	Oakite Products 22 Thames St. New York, N.Y.	2/20/51	McC	H.L. Fray, Vice-Pres.
72.	Onyx Oil & Chem. Co. 190 Warren St. Jersey City, N.J.	3/16/51	L.S.	Philip Kaplan, Pres.
73.	Oronite Chemical Co. 38 Sansome Sts. San Francisco 4, Calif.	9/28/50	McC	T.G. Hughes, Pres.
74.	Peerless Chemical Co. 3850 Oakman Blvd. Detroit 4, Mich.	12/4/50	McC	S.J. Caplan, Pres.

NAME OF COMPANY (PROJECT 86)	Date	By	Man Interviewed
75. Petrolite Corp. 30 Broad St. New York 4, N.Y.	2/28/51 (Letter)	McC	D. Drescher, Sec. & J.S. Lyall
No information of interest			
76. Pittsburgh Plate Glass Pittsburgh, Pa.	11/28/50	McC	Paul H. Croll - Ass't. to President
77. Procter & Gamble Co. Gwynne Bldg. Cincinnati 1, Ohio	3/13/51	McC	P.L. Blair, Dir. of Chem. Div. R.A. Duncan, Assoc. Dir. of Pur. Dept.
78. Quaker Chemical Products Conshohocken, Pa.	12/9/50	McC	D. Jacques Benolier, Pres. (Letter)*
79. Research Lab. Eastern Philadelphia, Pa.	11/7/50	McC	Drs. W.C. Ault, D. Swern R.W. Riemenschneider
80. Research Lab. Southern New Orleans, La.	12/9/50	McC	Dr. A.S. Markley (Letter)*
81. Research Lab. Northern Peoria, Ill.	12/19/50	McC	Dr. J.C. Gowan
82. Research Lab. Western Albany, Calif.	9/28/50	McC	Dr. A.B. Kester
83. Refined Products Corp. 624-34 Schuyler Ave. Lyndhurst, N.J.	No/		
84. Richards Chemical Works (See onyx 111) Jersey City, N.J.			
85. Rohm & Haas Co. Washington Sq. Philadelphia 5, Pa.	No/	McC	D.F. Murphy (Information not available)
86. Schenectady Paint & Varnish Company Schenectady, N.Y.	No/		
87. Schulderberger, W. P.O. Box 476 Baltimore 3, Md.	11/3/50 No	McC	W.F. Schluderberg, Pres. (Letter)*
88. Searle & Co. Chicago, Ill.	11/24/50 No	McC	Albert L. Raymond, Vice-Pres. (Cooperative but no work in field)

	NAME OF COMPANY (PROJECT 86)	Date	By	Man Interviewed
89.	Shell Development Co. (See Shell Chemical Co.) Emeryville, Calif.			
90.	Shell Chemical Co. RCA Bldg. 50 West 50th St. New York, N.Y.	9/19/50	McC	M.W. Leland, Mgr. of Economic Research Dept.
91.	Sinclair Refining Co. 630 Fifth Ave. New York 20, N.Y.	2/13/51	McC	L.W. Ison, Vice-Pres. in charge
92.	Sherwin-Williams Co. Newark, N.J.	3/14/51	L.S.	L.S. Stout, Chief formulator
93.	Smith, Werner G. Cleveland, Ohio	12/2/50	McC	F.C. Haas, Vice-Pres.
94.	Solvay Process Co. 40 Rector St. New York 6, N.Y.	3/7/51	McC	A.B. Blair, Tech. Sales Dev.
95.	Sonneborn, L. Sons, Inc. 88 Lexington Ave. New York 16, N.Y.	3/7/51	McC	A.A. Moscovitz, Chief Chem.
96.	Southern Research Inst. Birmingham, Ala.	9/18/50 No	McC	William M. Murray, Jr., Dir. (Letter)*
97.	Standard Oil of Ind. Whiting, Ind.	No		
98.	Swift & Co. Union Stock Yards Chicago, Ill.	12/13/50	McC Sills	E.A. Moss, Vice-Pres. V.J. Bullen, Mgr. - Tallow Dr. F.E. Lacey - Head of Oil M.R. Paylor - Plant Mgr. W.T. Cliphant, Sales Mgr.
99.	Tennessee Eastman Corp. Kingsport, Tenn.	11/14/50	McC	Dr. J.L. Magoffin
100.	Texas Co. Chrysler Bldg., New York 17, N.Y.	2/16/51	McC	Dr. W.E. Kuhn
101.	Ultra Chemical Works 2 Wood St. Paterson, N.J.	3/9/51	McC	Mr. Spuhle, Pres. A. Sharpouse F. Buck

Approved 15

NAME OF COMPANY (PROJECT 86) Date By Man Interviewed

102.	University of Illinois	12/20/50	McC	Dr. C. S. Marvel, Dept. of Chem.
103.	University of Minn.	12/7/50	McC	Dr. W. F. Geddes, Chief of Div.
104.	University of Iowa	No.		
105.	Lehigh University	11/27/50	McC	Dr. Johnson G. Small
106.	Stanford University			Dr. K. Brandt and Dr. Carl K. Moller (Letter)*
107.	University of Kentucky	No		
108.	State College, Penna.	11/28/50	McC	Dr. P. M. Althouse
109.	University of Pittsburgh Pittsburgh 13, Pa.	11/29/50	McC	Dr. B. F. Daubert
110.	U.S. Industrial Chem. 60 E. 42nd St. New York 17, N.Y.	2/26/51	McC	A. H. Gochrane, Sales Promotion
111.	Victor Chemical Works 141 W. Jackson Blvd. Chicago 4, Ill.	12/13/50	McC	D. B. Brower
112.	Warwick Chemical Div. 10-10 44th Ave. Long Island City, N.Y.	3/2/51	McC	Mr. Horn, Sales Div.
113.	Welch, Holme & Clarke 439 West St. New York, N.Y.	No		
114.	Werk & Co. St. Bernard Cincinnati, Ohio	3/13/51	McC	Mr. H. Dock, Technical Dir.
115.	West Disinfecting Co. Long Island City, N.Y.	3/2/51	McC	Dr. P. G. Bartlett, Chem. Dir.

475 FIFTH AVENUE NEW YORK 17, N. Y.

	NAME OF COMPANY (PROJECT 86)	Date	By	Man Interviewed
116.	Williams, J. B. Glastonbury, Conn.	3/27/51	McC	Dr. Guest, Chief Chemist T. Haugland, Plant Mgr.
117.	Winthrop-Stearns Inc. 170 Varick St. New York 13, N.Y.	12/4/50	McC	Aaron Edelston No cooperation
118.	Wilson & Co., Inc. 4100 S. Ashland Ave. Chicago 9, Ill.	12/11/50	McC	Wm. Day, Economist Jillie
119.	Woburn Chemical Corp. 1200 Harrison Ave. Harrison, N.J.	3/12/51	L.S.	Mr. Douglass, Gen. Mgr.
120.	Wurster & Sanger, Inc. 5201 S. Kenwood Ave. Chicago 15, Ill.	12/18/50	McC	H. J. Stockmann, Pres.
121.	Wyandotte Chemical Corp. Wyandotte, Mich.	12/4/50	McC	Wm. Day, Asst. to Pres.
122.	Formica Co. Spring Grove Ave. Cincinnati, Ohio	3/16/51	McC	Dr. J. D. Cochrane, Dir. of Res.
123.	R. T. Vanderbilt Co. 230 Park Ave. New York 17, N.Y.	3/23/51	McC	Dr. H. A. Saver, Res. Dept.
124.	Hooker Electro Chemical Niagara Falls, N.Y.	3/19/51	McC	H. B. Boyler, Sales Mgr.
125.	E. R. Squibb & Sons 745 Fifth Avenue New York, N.Y.	3/7/51	McC	Dr. Hanger, Dir. of Res. Lab.
126.	Packwood Mfg. Co. St. Louis, Mo.	12/21/50	McC	(No cooperation)
127.	Miranol Chemical Co. 16 Melville Place Irvington 11, N.J.	3/7/51	McC	H. C. Mannheim, Res. Dir.

	NAME OF COMPANY (PROJECT 86)	Date	By	Man Interviewed
128.	Kamen Soap Co. 233 Broadway New York 7, N.Y.	2/23/51	McC	A.L.Kamen, Pres.
129.	Tall Oil Association New York, N.Y.	3/9/51	McC	Mr. Avery, Secretary-Treas.
130.	Goldschmidt Chemical Co. 153 Waverly Place New York 14, N.Y.	2/27/51	McC	M.Habler, Mgr.
131.	Clifton Chemical Co. 62 Williams St. New York, N.Y.	1/26/51	McC	M. Backrack, Mgr.
132.	Ind. Raw Materials Corp. 52 Wall St. New York 5, N.Y.	2/26/51	McC	J. Newland, Gen. Mgr.
133.	Mathieson Chemical Co. Mathieson Bldg., Baltimore 3, Md.	3/26/51	McC	E.F.Woodward, Dev. Eng.
134.	Buffalo Electro Chem. Co. Buffalo 7, N.Y.	3/21/51	McC	Dr. R.P.GreenSPAN, Res. Chem

McC- J.J.McCutcheon
L.S. L. Sternberg (assistant)
Sills, M.Sills, (USDA, Observer)

* Letter indicates, generally, an exchange of correspondence and reply to questionnaire.

/ "No" means that company was on original list but not contacted for a variety of reasons. In most cases the company had no information to offer or disclose on the subject matter to hand as expressed by an exchange of letters.

INTERVIEW OUTLINE
AND QUESTIONNAIRE

RESEARCH ON TALLOW AND ITS DERIVATIVES

PART 1. PROCESSES

General

1. Firm Name
2. Kind of Firm
3. Person interviewed Position
4. Date of interview By
5. Fields of research
 - (1) Patent or Ref.
 - (2) Patent or Ref.
 - (3) Patent or Ref.
6. Application of the process to tallow, grease or derived acids
.....
.....
7. Economic & Technical aspects in reference to
 - a. Raw materials
 - b. Labor
 - c. Yields
 - d. Capital cost of equipment
8. Economic & Technical aspects in reference to Quality
.....
.....
.....
9. Economic & Technical aspects in reference to New Products (List products here and discuss each under Part 2 following)
.....
.....
.....
10. Overall evaluation
.....
.....
11. Remarks:
.....
.....

PART 2. PRODUCTS

General

12. Firm Name
13. Kind of Firm
14. Person interviewed Position
15. Date of interview By
16. Products or Class of product (Use separate sheet for each new type or class)
 1. Patent or Ref.
 2. Patent or Ref.
 3. Patent or Ref.

- 17. Raw materials used with source and remarks on same
 - 1.
 - 2.
 - 3.
 - 4.
- 18. Basic equipment required for plant production
 - 1.
 - 2.
 - 3.
 - 4.
- 19. Characteristics of the product under
 - a) Physical
 - b) Chemical
 - c) Derivatives from product
 - d) Raw materials required for production of derivatives from product
 - e) Basic equipment required for plant production of derivatives
 - 1.
 - 2.
 - 3.
 - 4.

PART 3. NEW APPLICATIONS

- 20. New Applications of established products (For example the extended use of the sodium salt of an alcohol sulfate for street cleaning, or the use of lithium oleate in lubricants or the increased use of tallow derived alcohol sulfates in retail detergents)
 - 1.
 - 2.
 - 3.
- 21. Applications of New Products
 - (a) Possible uses of prime product under Part 2-16 (under normal competitive conditions)
 - 1.
 - 2.
 - 3.
 - (b) Possible users of prime product by industry (under normal competitive conditions)
 -
 -
 -
 - (c) Main competing products that are already available in each field of use
 - 1.
 - 2.
 - 3.
 - (d) Remarks covering evaluation and supporting data where available
 -
 -
 -

(e) Characteristics, function and application of derivatives under Part (c) above.

	<u>Characteristics</u>	<u>Function</u>	<u>Field of Application</u>
1.			
2.			
3.			
4.			

(f) GENERAL REMARKS:

.....
.....
.....
.....

PART 4. LARD AND EDIBLE TALLOW

22. Firm Name
23. Kind of Firm
24. Person interviewed Position
25. Date of interview By
26. Edible Tallow and Lard produced by Type and Grade

<u>Edible Tallow</u>	<u>Range of Prod.</u> <u>in 1949*</u>	<u>Lard</u>	<u>Range of Prod.</u> <u>in 1949*</u>
1.		1.	
2.		2.	
3.		3.	
4.		4.	
5.		5.	
6.		6.	

Total lbs. Total lbs.

*Enter proper symbol, A= 0.-25,000 lb.: B= 25,000-50,000 lb.: C=50,000-100,000 lb.
D= 100,000 -1,000,000 lb. E= over 1,000,000 lbs.

27. Estimated distribution to consumers

<u>Edible Tallow</u>	<u>Percent of Total</u>	<u>Lard</u>	<u>Percent of Total</u>
<u>Grade</u>	<u>in 1949</u>	<u>Grade</u>	<u>in 1949</u>
Retail		Retail	
Industrial		Industrial	
Other		Other	

28. What processes are used for each type and grade?
.....
.....
.....

29. How does the process affect the quality of the product?
.....
.....
.....

30. What is the selling price as of October 1, 1950 for
edible tallow and lard in tank cars

<u>Ed. Tallow</u>	<u>Grade</u>	<u>Price</u>	<u>Lard</u>	<u>Grade</u>	<u>Price</u>
1.			1.		
2.			2.		
3.			3.		

31. What is the price of edible tallow contract basis as of October 1, 1950?
.....
32. How is the stock packaged by type ?
- | | <u>Type</u> | <u>Package and Wt.</u> | <u>% in 1949</u> |
|----|-------------|------------------------|------------------|
| 1. | | | |
| 2. | | | |
| 3. | | | |
| 4. | | | |
| 5. | | | |
| 6. | | | |
33. To what do you attribute the more favorable acceptance for the more expensive edible fats, such as hydrogenated vegetable shortening than for edible tallow and lard?
.....
.....
34. What can be done to develop a more favorable acceptance of edible tallow and lard?
.....
.....

PART 5.

35. Firm Name
36. Kind of Firm
37. Person interviewed Position
38. Date of interview By
39. What lines of fundamental research in your opinion would be most beneficial to your operation?
.....
.....
.....
.....
40. What lines of fundamental research in general would appear most promising with respect to increased utilization of inedible animal fats
.....
.....
.....
.....
.....

2

NATIONAL AGRICULTURAL LIBRARY

1022344012

NATIONAL AGRICULTURAL LIBRARY



1022344012